
Diesel Exhaust Emissions Control for Light Duty Vehicles

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ABSTRACT

The objective of this paper is to present the results of diesel exhaust aftertreatment testing and analysis done under the FreedomCAR program. Nitrogen Oxides (NO_x) adsorber technology was selected based on a previous investigation of various NO_x aftertreatment technologies including non-thermal plasma, NO_x adsorber and active lean NO_x. Particulate Matter (PM) emissions were addressed by developing a catalyzed particulate filter. After various iterations of the catalyst formulation, the aftertreatment components were integrated and optimized for a light duty vehicle application.

This compact exhaust aftertreatment system is dual leg and consists of a sulfur trap, NO_x adsorbers, and catalyzed particulate filters (CPF). During regeneration, supplementary ARCO ECD low-sulfur diesel fuel is injected upstream of the adsorber and CPF in the exhaust. Steady state and transient emission test results with and without the exhaust aftertreatment system (EAS) are presented. Results of soot filter regeneration by injecting low-sulfur diesel fuel and slip of unregulated emissions, such as NH₃, are discussed. Effects of adsorber size and bypass strategy on NO_x conversion efficiency and fuel economy penalty are also presented in this paper. The results indicate that if the supplementary fuel injection is optimized, NH₃ slip is negligible. During the FTP cycle, injection of low sulfur diesel fuel can create temperature exotherms high enough to regenerate a loaded CPF. With the optimized NO_x adsorber regeneration strategies the fuel injection penalty can be reduced by 40 to 50%. Results for various other issues like low temperature light off, reductant optimization, exhaust sulfur management, system integration and design trade-off, are also presented and discussed in this paper.

INTRODUCTION

Due to their excellent fuel efficiency, reliability, and durability, compression ignition direct injection (CIDI) engines have been used extensively to power almost all highway trucks, urban buses, off-road vehicles, marine carriers, and industrial equipment. CIDI diesel engines burn 35 to 50 % less fuel than gasoline engines of comparable size, and they emit far less greenhouse gases (Carbon dioxides), which have been implicated in global warming. Although the emissions of CIDI diesel engines have been reduced significantly over the last decade, there remains concern with the NO_x and PM emissions levels. In 2000, the US EPA proposed very stringent emissions standards to be introduced in 2007 along with low sulfur (< 15 PPM) diesel fuel. The California Air Resource Board (CARB) has also established the principle that future diesel fueled vehicles should meet the same low emissions standards as gasoline fueled vehicles and the EPA followed suit with its Tier II emissions regulation.

Meeting the Tier II standards requires NO_x and PM emissions to be reduced significantly. Achieving such low emissions cannot be done through engine development and fuel reformulation alone, and requires application of NO_x and PM aftertreatment control devices. This paper provides a summary of the study of an integrated engine and aftertreatment system for achieving very low vehicle-out emissions while maintaining the superior advantages of CIDI on fuel efficiency, reliability, and durability.

EMISSION STANDARDS AND TEST CYCLE DEFINITION

Based on EPA's Tier 2 emission standards that will be phased-in between 2004 and 2009, vehicles are classified based on gross vehicle weight rating (GVWR), and their applications. Passenger cars and light-duty trucks with GVWR less than 8500 lb. are tested on

chassis dynamometer using FTP-75 cycle and Supplemental Federal Test Procedure (SFTP). Heavy-duty vehicles with GVWR above 8500 lb. are tested on engine dynamometer using FTP Heavy Duty (HD) cycle and Supplemental Emission Test (SET). Medium-duty passenger vehicles (MDPV) for GVWR up to 14,000 lb. can be optionally tested using either light-duty standards or heavy-duty standards.

FTP-75 cycle specifies the vehicle speed over time, and emission standards in g/mile. Three phases are included in this cycle: 0-505 sec cold transient, 506-1372 sec cold stabilized, and 0-505 sec hot transient. The hot transient phase is a repeat test of the cold transient phase, but with a 10-min soak period following the cold stabilized phase. Emissions from cold and hot start are combined using the weighting factors of 0.43 and 0.57, respectively, with an assumption that the stabilized cold phase will have the same emissions as the hot start. Following Tier 2 standards, vehicle manufacturers will have a choice to certify a specific vehicle to any of the 8 bins of different stringency. However, the entire vehicle fleet sold by each manufacturer will have to meet the average NO_x and PM standards of 0.07 gm/mile and 0.01 gm/mile respectively.

US HD cycle specifies the normalized engine speed and torque history with respect to full-throttle torque curve, and the emission standards in g/bhp-hr. There is a 20-min cold start transient cycle, followed by a repeat 20-min hot start transient cycle after a 20-min soak period. Unlike FTP-75 cycle, the cold start emission has a much lower weighting factor, 1/7 vs. 6/7, for the hot start cycle. For US HD transient cycle, the NO_x and PM standards of 0.2 gm/bhp-hr and 0.01 gm/bhp-hr respectively, will be phased in between 2007 and 2010. Additionally, SET emission test using Euro III cycle will be met against the same FTP standard, and Not-to-Exceed (NTE) to meet 1.5 times the FTP standards.

APPROACH

Under this study, various aftertreatment technologies including NO_x absorbers, catalyzed particulate filter, and sulfur trap, in conjunction with active reductant injection were investigated and developed for emission control subsystem integration and development [1]. The areas of NO_x adsorber development include catalyst formulation for high conversion over an increased catalyst/exhaust gas temperature range, catalyst structure for increased exhaust gas residence time on active catalyst sites, and an understanding of the various factors that cause deactivation of the catalyst. Fuel reformulation concepts were investigated to increase the activity of the hydrocarbons introduced into the catalyst systems. Even with the availability of 15 ppm sulfur fuels, the development of a sulfur management scheme is critical to prevent catalyst poisoning and deactivation. The application of a sulfur trap that can be regenerated offline or periodically replaced was explored.

PM emissions were addressed by developing a CPF. The key areas of development include developing catalyst formulation with improved low temperature performance, exploring synergies between particulate

and NO_x aftertreatment strategies, and determining the need for supplemental heating. A supplemental heating system may be required to help the CPF get through those portions of the duty cycle where temperature is too low to achieve a high rate of particulate burning to prevent soot accumulation.

Finally, the improved aftertreatment components were integrated and configured optimally in a system developed for a light duty application. This system was calibrated and tested in a controlled environment on a light duty sized engine.

AFTERTREATMENT DEVICE FUNDAMENTAL AND FORMULATION DEVELOPMENT

NO_x adsorber technology relies on removal of NO_x from the exhaust under lean conditions by adsorption [2]. This is followed by periodic regeneration of the adsorbent along with reduction of the released NO_x under rich conditions. This alleviates the need for maintaining a given C1/NO_x ratio under transient and fluctuating exhaust NO_x levels, as in the case of the lean NO_x catalyst. For current state-of-the-art catalysts the lean adsorption step entails the reaction of an acidic gas (NO₂) with a basic adsorbent (alkaline earth oxide, e.g. BaO) to form a nitrate or nitro-species. Since engine-out NO_x is primarily (90%) NO it must first be oxidized to NO₂ over a Pt-based catalyst. The results indicate that Pt/Base Metal Oxide (BMO) intimate contact is essential for higher NO_x trapping capacity. When the effective capacity of the adsorber is reached, the NO_x is released by a pulsed introduction of hydrocarbon (HC) reductant (e.g. diesel fuel) enough to establish a rich environment and under this condition the NO_x is reduced to N₂ over a conventional three-way catalyst. Nitrate or adsorbed NO₂ can decompose and desorb from BMO thermodynamically, and it is O₂ partial pressure dependent. NO_x can also desorb by HC displacement, partially due to incomplete reduction. Trapped NO₂ can totally desorb in the absence of O₂ at 450 deg C. The Pt/BMO interface is essential for NO_x reduction to N₂ with reductants during rich operation. No reduction of trapped NO_x was observed on BMO without Pt. Experimentally it was determined that the reductant quantity, at least 2 times of stoichiometry of CH₂ is needed for full regeneration, and insufficient reductant leads to NO formation. Trapped NO_x quantity also affects the NO_x reduction, loosely trapped NO_x species tend to release as NO during regeneration. The reduction reaction is kinetic controlled. It depends on reductant type, reduction temperature, especially at low temperature (e.g. <250 deg C), and reduction time.

With regard to PM control technology, CPF has been successfully formulated for HD diesel application, which achieves passive regeneration. Nevertheless, the passive filter regeneration is not robust, especially in cold climates. Typically, application screening must be performed prior to installing the particulate filter on the vehicle, and at least 10% of the duty cycle must be spent with filter inlet temperatures above 315 C. In addition,

one must balance between particulate loading rate, engine duty cycle, filter size, and ambient temperature.

Another characteristic of passive regeneration of particulate filters is uncontrolled regeneration. Uncontrolled regeneration of particulate filters can occur when the filter is loaded with particulates, and undergoes an event during the duty cycle that initiates particulate combustion in the filter. After the particulate begins to combust, if the duty cycle is such that the vehicle goes to a stop, idle, or engine motoring condition, producing a low flow exhaust condition, the filter may overheat, and uncontrolled regeneration and subsequent filter failure will occur. The main factors that influence uncontrolled regeneration of particulate filters include: particulate loading level, exhaust temperature, exhaust flow, O₂ concentration, NO₂ concentration, and catalyst formulation. Engine results have shown that low precious metal loaded filters are more prone to undergo uncontrolled regeneration than filters with high levels of precious metals. This is directly related to the slower particulate burning rates associated with low precious metal loaded filters.

Critical experiments were designed to investigate the selected CPF system further. An advanced catalyzed particulate filter was tested with a precat upstream to evaluate the advantage of NO to NO₂ function and catalyst exotherm in terms of balance point temperature (BPT). The precat with the advanced CPF gave a 40 to 50 C reduction in the balance point temperature and better regeneration performance. The benefits of using a catalytic system for particulate filter regeneration are many: it is a relatively simple system, low cost, and has synergistic opportunities with the rest of the aftertreatment system. For instance, the CPF can be placed downstream of the NOx adsorber to make use of the heat generated during regeneration of the NOx adsorber. In this configuration, the CPF can also make use of the HC slip across the NOx adsorber, which will cause an additional exotherm with the CPF itself.

EXHAUST SULFUR MANAGEMENT

The NOx adsorber catalysts have achieved high NOx reduction levels using very low sulfur (< 3 ppm) diesel fuels. However, the degradation of adsorber performance due to sulfur poisoning remains an issue and needs to be addressed [3,4]. SOx competes for active NOx adsorption sites to form thermodynamically stable compounds that require an extremely high temperature (> 650 C) and reductant to regenerate the adsorber. The testing indicate that even with the availability of 15 ppm sulfur diesel fuels, an effective exhaust sulfur management scheme is required to keep emission control devices operating near their peak effectiveness.

There are two paths that are currently being explored for sulfur management: (1) the use of SOx trap that can be regenerated offline or replaced periodically, and (2) the use of diesel fuel and high temperature to desorb the sulfates from NOx adsorber. The Pros and Cons of each system are summarized below.

Disposable/Offline Regenerable

- High adsorption capacity for sulfur
- High selectivity toward sulfur adsorption
- No release of secondary emissions from trap
- Usable life of SOx trap is dependent on Sulfur level in fuel and lube oil
- Good protection of adsorber catalyst from sulfur poisoning during miss-fueling
- Good technology for light duty applications-small size, low cost, and limited useful life requirement

NOx Adsorber Desulfation Catalyst

- Integrated NOx trap and sulfur trap function on one catalyst, does not require separate SOx trap
- Requires on-board high temperature exhaust management to release sulfur from catalyst (>600 C)
- Additional fuel penalty will be incurred during desulfation process
- Desulfation involves release of secondary emissions hydrogen sulfide and/or sulfur dioxides
- Catalyst material development required compromise among NOx storage & conversion, SOx storage & release, and catalyst thermal durability etc.

SYSTEM INTEGRATION AND DESIGN TRADE-OFF

Issues related to design trade-off, such as, effect of catalyst size, effect of target air-fuel ratio, effect of lean time and effect of bypass strategy are discussed in the following.

EFFECT OF CATALYST SIZE

The effect of catalyst size on NOx conversion efficiency and fuel penalty for full flow (FF) regeneration was studied under the control-based strategy at steady state. In FF, the whole exhaust flows through the catalyst during lean as well as rich operation. Under control based strategy the catalyst is regenerated only when the efficiency falls below the target value. The catalyst inlet temperature was varied by changing the engine torque. The NOx concentration was different at each temperature and depended on engine calibration. The Figure 1 shows the effect of catalyst size on NOx conversion efficiency and fuel penalty. The testing was done on a 5.9 L mule engine and the NOx adsorber catalyst size was varied from 7 L to 21 L. As shown, 10.5 L catalyst (~1.8 times engine displacement) can achieve the same NOx conversion efficiency as catalysts of bigger volume. The fuel penalty is similar above 320 °C for all tested catalyst sizes. Below 320 °C, fuel penalty becomes higher for smaller catalyst sizes. A 7 L NOx adsorber has the worst NOx conversion efficiency and fuel penalty, and is inadequate for the application.

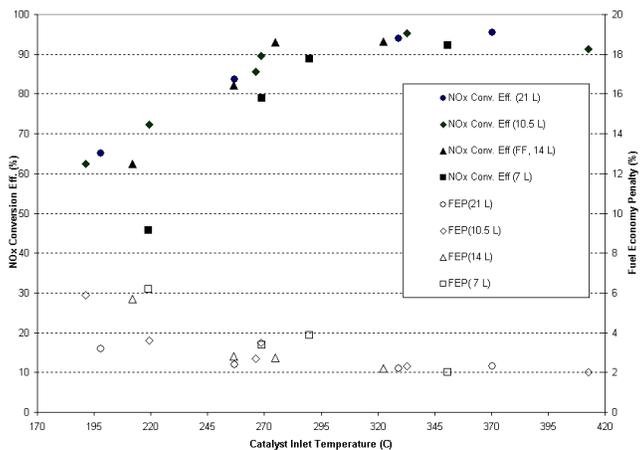


Fig 1 Effect of catalyst size under control-based regeneration at Steady State

EFFECT OF A/F RATIO AND LEAN TIME

Under steady-state engine operating conditions, the NOx adsorber is normally regenerated at fixed time intervals, for example, every 30 seconds. The quantity of the injected fuel has to be sufficient not only to produce rich conditions ($\lambda < 1$), but also to react with NOx desorbed from the catalyst and convert it into N_2 [6]. To ensure this condition is met, the injection quantity is usually based on a target air/fuel (A/F) ratio lower than stoichiometric (14.6 for diesel fuel), such as A/F=9. For diesel engines operating in oxygen rich exhaust conditions ($\lambda > 1$), a significant portion of the injected fuel is used to consume O_2 in the exhaust. While laboratory tests have shown that a longer regeneration period can improve regeneration efficiency, this is usually not practical due to proportionally higher fuel penalty associated with the O_2 reaction. For this reason, fuel injection is typically limited to produce only a very short rich period, for about 1 to 2 seconds. The effectiveness of the injected fuel to produce conditions favorable for NOx conversion depends on many factors, such as fuel atomization, injection quantity (A/F ratio) and flow distribution.

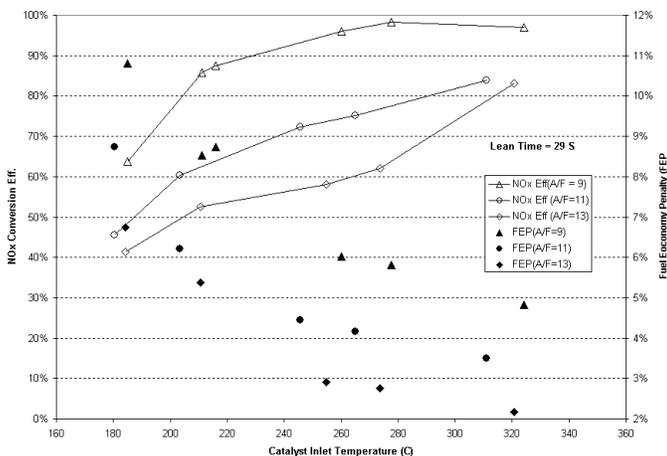


Figure 2 Effect of Target A/F Ratio

In this study, the NOx adsorber catalyst volume was 14 L and the target A/F ratio were varied from 9 to 13 to study its effect on NOx conversion efficiency. Figure 2 shows the effect of target A/F ratio on NOx conversion efficiency and fuel penalty at fixed 29-second lean and 1-second rich time. As shown, both NOx conversion efficiency and fuel penalty increase with decreasing A/F ratio target. A/F ratio of 9 will be needed to achieve the high NOx conversion efficiency necessary to meet tier II emissions. The actual A/F ratio was within 5% of target A/F ratio.

Figure 3 shows the NOx conversion efficiency using different lean times against varying catalyst inlet temperature. The target A/F ratio is fixed at 9 for 1-second. As noted, high NOx conversion efficiency can be obtained by using either 29-second or 20-second lean time. But the latter has higher fuel penalty due to higher regeneration frequency. The NOx conversion efficiency starts to deteriorate when the lean time increases from 29 s to 40 s.

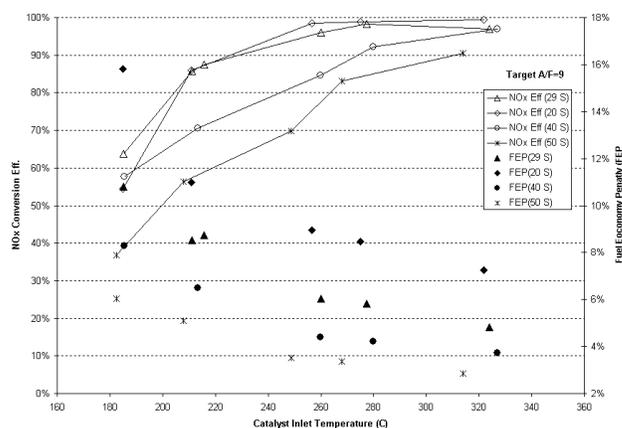


Figure 3 Effect of Lean Time

BYPASS STRATEGY

One way to reduce fuel penalty associated with NOx adsorber regeneration is to reduce O_2 flow during regeneration. This can be accomplished by using the bypass configuration as shown in Figure 4. In the full bypass (FB) system the flow after the SOx trap is split equally into two bypass legs. Each leg contains one-half of the total NOx adsorber volume, and each has a fuel injection system in front of the adsorber for regeneration. There is a CPF downstream after the two-leg combine. During regeneration, the flow through the adsorber under regeneration is restricted to below 50% of the total engine exhaust. For a fixed catalyst-in A/F ratio target, the fuel injection required for regeneration can be proportionally reduced. For example, when 80% of the flow is bypassed during regeneration, the total fuel penalty is reduced by 60% when compared to full-flow regeneration. In addition, tests have shown that the HC slip after the NOx adsorber is also lower. This is because space velocity and fuel injection quantity are both lower during bypass, resulting in more complete reaction.

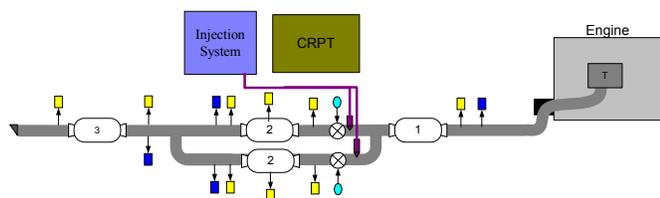


Figure 4 Schematic of Full Bypass System

Testing under this program has confirmed that for the same NO_x conversion efficiency the fuel penalty for FB is about 50~60% lower than for FF. In addition, the hydrocarbon slip from FB is much lower than FF because of the lower space velocity during regeneration period in FB system.

TRANSIENT CVS TESTING

The integrated aftertreatment system transient testing was carried out using the breadboard ISB 5.9 L engine in a CVS test cell. Simulated FTP-75 cycle was obtained from computer simulation and validated in chassis dynamometer tests of a typical Dodge Ram vehicle. Arco EC-D low sulfur (< 15 ppm) diesel fuel was used for both the breadboard ISB engine and the exhaust injection. A 7 L SO_x trap, two 14 L NO_x adsorbers and a 12.5 L CPF were arranged as shown in Figure 4. Two exhaust valves are used, one on each leg of the bypass system, to regulate the bypass flow. For the full flow configuration the adsorbers were arranged in series.

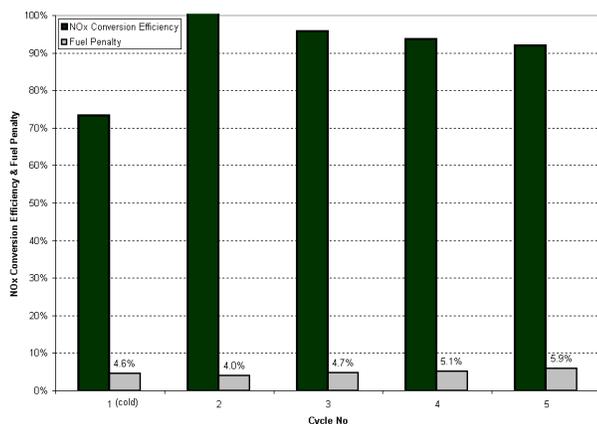


Figure 5 NO_x conversion efficiency and fuel penalty for simulated FTP cycle

As compared to steady-state tests, transient tests provide some additional challenges. For example, the turbo out temperature is lower than the steady-state operation of the same engine speed and load due to engine thermal inertia. The effect of thermal inertia of the aftertreatment system also becomes more important, and further reduces the peak temperature at catalyst inlet. The initial state of the NO_x adsorber is unknown at

the beginning of each FTP-75 cycle. For steady-state tests, this can be overcome by a period of stabilized catalyst operation. It is impractical to pre-determine the regeneration timing and injection quantity, especially in real-world applications where the exhaust flow condition is varying continuously. Additionally, for bypass regeneration, the two catalysts can experience different inlet conditions (NO_x rate, temperature, etc.), as well as different initial states.

A closed-loop regeneration control algorithm using various sensor inputs is implemented on a programmable controller. The regeneration timing and injection quantities are both dynamically determined by the controller during the transient test. To illustrate the impact of the initial state, the NO_x adsorbers were first conditioned at a favorable steady-state condition (1400 rpm, 200 ft-lb). Subsequent to the pre-conditioning, a hot FTP cycle was run without exhaust fuel injection. Over 90% NO_x conversion efficiency can be obtained with no fuel penalty. However, this high efficiency can not be sustained. When the tests were repeated without pre-conditioning and regeneration, the NO_x conversion efficiency dropped to around 70%, and then 50%, as the initial NO_x loading at the beginning of each cycle became higher.

Since the NO_x adsorber is a storage device, it is necessary to demonstrate the effectiveness of regeneration by maintaining the NO_x conversion efficiency over several FTP cycles without pre-conditioning. The final state of these hot FTP cycles can be used to start the cold FTP-75 cycle the next day. Because of the low exhaust temperature, 72% NO_x conversion efficiency was obtained for the cold cycle (Figure 5). For subsequent hot FTP-75 cycles, the NO_x conversion efficiency averaged about 87%. The CPF particulate trapping efficiency averaged about 93%. At about 200 seconds, there is a drop in the cumulative NO_x efficiency because a period of high space velocity and high NO_x loading occurs when the catalyst temperature is still relatively low. Subsequent regeneration slowly recovers the NO_x conversion efficiency to the final value.

CHASSIS DYNAMOMETER TESTING

To evaluate the performance of an integrated aftertreatment system designed for a light duty vehicle, testing was conducted on the chassis-dynamometer at Argonne National Laboratory (ANL). The full bypass NO_x adsorber system with exhaust injection was fitted to a Mercedes A170 vehicle, and several parameters including engine and tailpipe emissions, and catalyst efficiency were monitored. To prevent Sulfur poisoning, a sulfur trap upstream of the adsorbers was used during the testing in conjunction of the 15-ppm ARCO ECD low sulfur fuel. A catalyzed particulate filter (CPF) was used to reduce system-out particulates and hydrocarbon emissions (Figure 6).



Figure 6 Full bypass EAS at ANL

To characterize the operation and efficiency of the catalyst system, every emissions bench within the Argonne lab was used. In total, a raw exhaust bench, two fast-response hydrocarbons, two fast-response nitric oxide, a particulate sampler, and a dilute bench with CVS were utilized. These emission measurement systems allowed for continuous monitoring of engine out emissions, catalyst efficiency, tailpipe out emissions and fuel consumption. The A170 is a 1.7 L engine and has about 0.9 g/mile engine out NOx. Table 1 shows the catalyst volumes used in the EAS. The NOx adsorber catalyst volume to engine displacement was selected to be 1.8 based on the system design tradeoff critical experiment discussed earlier. The total catalyst volume to engine displacement was 4. The baseline vehicle performance was evaluated first and is shown in Table 2. This was collected with additional 2" Hg backpressure to account for the EAS.

performance. Glow plugs were used to simulate engine management for exhaust temperature enhancement. Different injectors with improved atomization were also tested.

Table 1

Catalyst	Volume, L
SOx	1.25
Adsorber	3.1
CPF	2.5
Total	6.85

Table 2

Cycle	CO	CO ₂	THC	NOx	mpg
UDDS	1.28	223	0.081	0.957	44.9
HFET	0.62	176	0.035	0.787	57.3

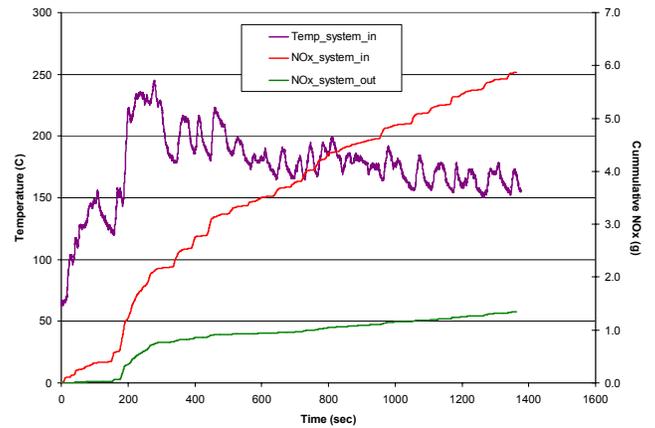


Figure 8 Representative UDDS cycle results

A representative UDDS cycle result is shown in Figure 8. The majority of the NOx slip from the aftertreatment system occurred around the 200-second hump in the UDDS cycle. A NOx conversion efficiency of 99 % was obtained with a preconditioned catalyst. Preconditioning was done by running the vehicle at 65 miles per hour for 5 minutes while doing reductant injection. Without preconditioning a NOx conversion efficiency of 89% could be achieved at about 11.6 % total fuel penalty for the FTP-72 cycle. The PM conversion was close to 99% and was beyond the detection capability of the measurement system at ANL.

Synergistic effects of NOx adsorbers and particulate filters were evaluated by attempting to regenerate CPF using HC injection. The initial steady state results (Figure 9) indicate that CPF can be regenerated using HC injection. At the start of the test the CPF was loaded (13" of water delta pressure). Hydrocarbon (diesel fuel) was injected upstream of the NOx adsorber which raised the system inlet temperature of 200 °C to almost 400 °C at CPF-in and the CPF was back to its originally clean condition in less than 10 minutes.

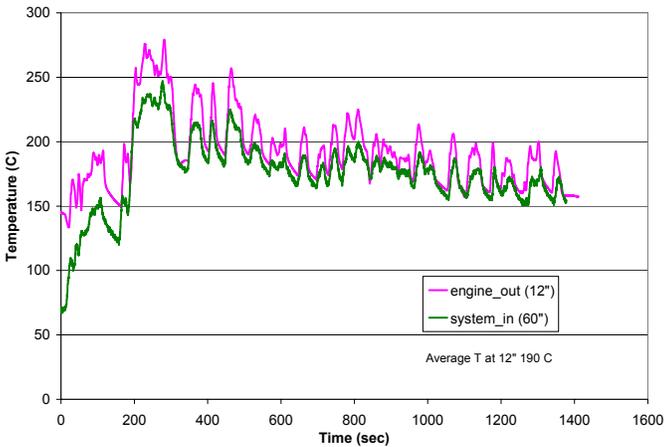


Figure 7 Temperature histories over UDDS cycle

The temperature history over the Urban Dynamometer Driving Schedule (UDDS) cycle is shown in Figure 7. As can be seen the temperature was very cold over the cycle, generally below 200 C. Various control algorithms and hardware were tested to obtain the best system

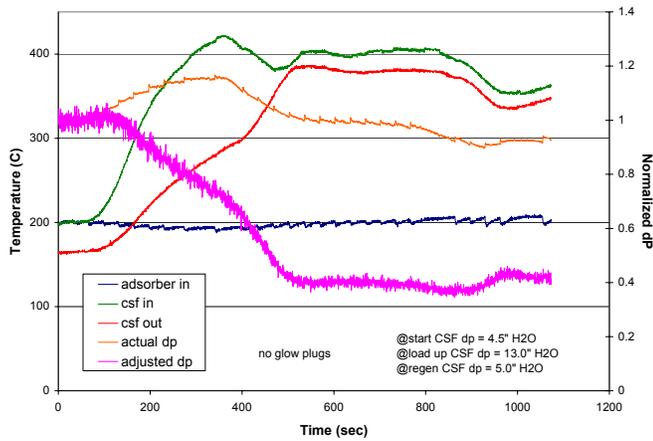


Figure 9. Catalyzed particulate filter regeneration using HC injection

There has been some speculation that NH_3 is formed over the adsorber catalyst when HC is injected for cleaning up the stored NO_x . A simulated cycle, which closely resembled the temperature distribution of an FTP-72 cycle, was run. When the reductant injection was too frequent (e.g. every 20 seconds) considerable amount of NH_3 was formed with each injection. When the injection frequency was reduced (keeping the injection quantity per shot the same) the NO_x conversion efficiency did not reduce substantially indicating more frequent injection was unnecessary fuel penalty. Excess HC was resulting in substantial NH_3 formation and slip. This result is shown in Figure 10.

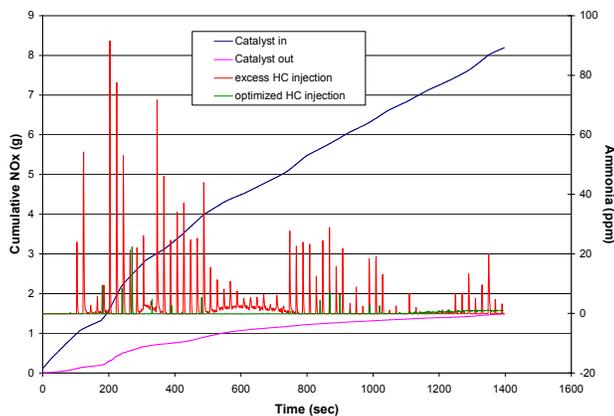


Fig. 10 NH_3 Slip from Aftertreatment system

This testing showed that NH_3 does form over the adsorber but it seems to be a secondary reaction to HC combustion and NO_x reduction. If HC is still left after these reactions, it may form NH_3 if conditions are right for that reaction. So if the control strategy is well defined to avoid over injection, NH_3 formation may not be a problem.

Based on the target AF ratio for these tests, the O_2 in exhaust was supposed to be close to zero after each injection. However, the oxygen does not drop to the low levels in the exhaust always. It was noticed that the NH_3 spike was higher every time the HC combustion efficiency was high (oxygen in exhaust was less). It was also noticed in this testing that NH_3 formation was

proportional to HC injection quantity. As can be seen in the figure, very little NH_3 is formed when the HC injection is optimized. NH_3 spikes are still seen around 200 sec in the cycle. These spikes are believed to be due to the stored HC over the first 200 seconds.

LOW TEMPERATURE LIGHT-OFF AND REDUCTANT SCREENING

Progress has been made on the adsorber formulation development [1]. The engine test results indicate that the NO_x conversion vs. temperature curve has extended the operation of catalysts by about 50 to 100 C lower as compared to the previous formulations. However, due to diesel fuel oxidation limitations, the low temperature light-off of an adsorber may not be expected below 200 C. Two alternatives have been analyzed to improve low temperature conversion of NO_x adsorbers, (1) using a reformer to generate reductants, which can operate at lower temperatures and (2) to raise exhaust temperatures so that diesel fuel may be used directly as the reductant. An analysis tool was used to compare the fuel economy penalty between the cases where a reformer is used vs. exhaust temperature enhancement. The reformer produces hydrogen and carbon monoxide, which are active reductants even at 180 C while diesel is active only above 200 C. The reactor test results indicate that H_2 is the best reductant, followed by a mixture of H_2 and CO , followed by CO . Short straight chain ($\text{C}_4\text{-C}_8$) hydrocarbons are not good reductants for adsorber catalyst (Figure 11).

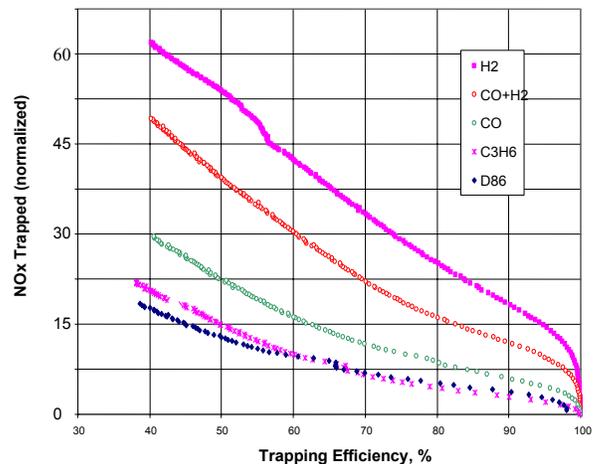


Fig. 11 Effectiveness of different reductants on adsorber trapping capacity

For low temperature operation of NO_x adsorbers, either a reformer can be used or the exhaust temperature may be raised by 20 C. Analytical results show using the catalytic partial oxidation (CPO) reformer will require about 2% fuel penalty to keep it running, and the total fuel penalty for the reformer option will be almost 7% as compared to 5% for exhaust temperature enhancement [5].

Using a CPO reactor the feasibility of using diesel fuel to generate the syngas and use as the reductant was evaluated. The CPO was hooked upstream of the

catalyst. During this initial testing Naphtha (Carbon Number chemistry from C7- C10) was used to generate the syngas. During the regeneration cycle the engine exhaust was bypassed 100% and only the reformat (syngas) flowed through adsorber catalyst. GC analysis showed 30% H₂ and 17% CO in the dry reformat. A NO_x conversion of greater than 90% was demonstrated for inlet exhaust temperatures ranging from 148 C to 448 C.

CATALYST DEGRADATION

Catalyst durability is the most critical issue for current aftertreatment systems using NO_x adsorber technology. Spectroscopic characterization of the inlet portion of catalyst samples following the time sequence of an engine test revealed important information related to catalyst deactivation. Deactivation of NO_x adsorbers involves many pathways and S-poisoning is possibly the most recognizable one. The degradation pathways that have been identified under this program are summarized in Figure 12.

Adsorber degradation mechanisms				
	Chemical	Thermal	Mechanical	Capability/Tool
Adsorption	S poisoning (fuel/lube) Lube/ash poisoning Carbonaceous deposits (coking) Condensation/solubility of metal nitrate	Pt & Metal-Oxide sintering	Physical breakage	Surface Analysis DRIFTS Lube oil tests Reactor
Regeneration	Residual nitrate Physical/chemical blockage of pores	Pt-MO interactions MO-support interactions		SpacIMS DRIFTS
Conversion	Poison-induced reconstruction of catalyst surface	Pt & MO sintering		Surface Area Platinum Dispersion
Desulfation	Residual sulfate	Pt & MO sintering Pore / surface changes	Thermal shock	Reactor Engine Tests

MO = Metal Oxide

Figure 12 Catalyst Degradation Mechanisms

Surface changes on catalysts can be characterized using differential DRIFTS, a subtraction of the spectrum of the fresh sample from the spectrum of an aged sample. Both buildups and depletions are observed in differential DRIFTS. The assignment of the condensed hydrocarbons can be verified by Raman spectra between the fresh and the aged sample. For aged samples, the fluorescence comes from the aromatic residual of the condensed hydrocarbon species. The intensity ratio between these two carbon bands reflects the aromatic domain size. It is a good indicator of formation of coke precursor. Temporal buildups of nitrates, sulfates and hydrocarbons were also studied. Nitrate buildup seems to slow down after 200 hrs of operation. Besides a rapid increase at the beginning, the sulfate buildup increases continuously in intensity with time. Further reactions of surface oxy-sulfur species to form pyro- or poly-sulfates may account for the continuous buildups. The overall buildups of hydrocarbons also grow with time. However, the non-uniformity of the burning of the injected fuel during operation gives rise to fluctuations in hydrocarbon deposit.

CONCLUSIONS

Results of extensive aftertreatment subsystem design and analysis to date indicate that the best NO_x control approach for LDV and LDT applications is NO_x adsorber technology. A greater than 84% combined NO_x reduction efficiency is required to achieve 0.07 g/mile NO_x vehicle-out emissions. An 84% NO_x conversion efficiency and 95% PM conversion efficiency has been demonstrated with a breadboard low emission Cummins ISB engine and an adsorber/CPF exhaust configuration on a simulated FTP-75 emission cycle at about 7% total fuel penalty. Encouraging NO_x conversion efficiency results were also obtained at ANL with the present EAS system. A NO_x conversion efficiency of 99 % can be obtained with a preconditioned catalyst. Without preconditioning a NO_x conversion efficiency of 89% could be achieved at about 11.6 % total fuel penalty for the FTP-72 cycle. The PM conversion was close to 100% and was beyond the detection capability of the measurement system at ANL.

With the lower exhaust temperatures encountered in Light Duty vehicle application, the improvement in NO_x conversion efficiency over a wider exhaust temperature range has also been identified as a critical development task. Significant progress has been made on adsorber formulation development, extending the operation of the catalysts by 50 to 100 C lower as compared to previous formulations.

Progress has also been made on NO_x adsorber regeneration strategies reducing the fuel injection penalty by 40 to 50% compared to earlier tests. There is some NH₃ production during adsorber regeneration but is not an issue if the HC injection is optimized. Heat release from HC injection for adsorber regeneration may be utilized to keep the CPF clean.

Throughout the project the emphasis has been on a fundamental understanding of aftertreatment technologies. Demonstrations have been focused on repeatable performance and development efforts have been directed towards technologies, which have a reasonable chance of meeting EPA anticipated regulations. Much has been accomplished to date, but much work remains in order to deliver the technology to marketplace.

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