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SELECTIVE CATALYTIC REDUCTION OF DIESEL ENGINE NOX EMISSIONS USING ETHANOL AS A REDUCTANT

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ABSTRACT

NO_x emissions from a heavy-duty diesel engine were reduced by more than 90% and 80% utilizing a full-scale ethanol-SCR system for space velocities of 21000/h and 57000/h respectively. These results were achieved for catalyst temperatures between 360 and 400°C and for C1:NO_x ratios of 4-6. The SCR process appears to rapidly convert ethanol to acetaldehyde, which subsequently slipped past the catalyst at appreciable levels at a space velocity of 57000/h. Ammonia and N_2O were produced during conversion; the concentrations of each were higher for the low space velocity condition. However, the concentration of N_2O did not exceed 10 ppm. In contrast to other catalyst technologies, NO_x reduction appeared to be enhanced by initial catalyst aging, with the presumed mechanism being sulfate accumulation within the catalyst. A concept for utilizing ethanol (distilled from an E-diesel fuel) as the SCR reductant was demonstrated.

INTRODUCTION

The use of hydrocarbons to reduce diesel exhaust NO_x emissions via selective catalytic reduction (SCR) has not been studied as extensively as urea-based SCR systems. Bench-scale evaluations of hydrocarbon-SCR (HC-SCR) have typically not demonstrated high efficiencies (greater than 80 percent NO_x reduction) for realistic space velocities (1). On the other hand urea-SCR was developed in the 1970s for stationary applications (including stationary diesel engines) and has consistently demonstrated NO_x reduction efficiencies greater than 90 percent when the SCR system operates in a favorable temperature window (2). In fact, urea-SCR is one of a few catalyst technologies capable of reducing diesel NO_x emissions to the 2007 NO_x limit of 0.2 g/bhp-hr (2).

There are also concerns with applying urea-based SCR to on-road vehicles, including 1) the need for a separate onboard tank for urea, 2) the infrastructure to supply urea, 3) residue buildup during inadvertent over-injection or injection at low temperatures, 4) corrosivity associated with urea, 5) high freeze point, and 9) the performance is best at optimum NO/NO_2 ratios which, in turn, require a pre-oxidation catalyst to maintain optimum NO/NO_2 ratios which can only be partially controlled using a pre-oxidation catalyst. Because of these concerns, there is a need for more convenient SCR systems, preferably those that use diesel fuel or a fuel-borne additive as the reducing agent. As a result, investigators have been pursuing new methods of HC-SCR.

HYDROCARBON SCR

Although the development of hydrocarbon-based SCR has not progressed as far as urea-based systems, catalysts utilizing hydrocarbon reductants have been developed and evaluated since the 1980s. The NO_x reduction efficiencies for HC-SCR have tended to be lower than for ammonia-based SCR systems (1, 3-7).

Of the HC-SCR systems studied, the alumina supported (highly-loaded) silver catalysts have been identified as one of the more promising NO_x control technologies for light-duty diesel emissions (1). Successful reducing agents include paraffins, alcohols, and aldehydes. In some cases, the conversion levels can be greater than 80% for the temperature range of 350 to 500°C and these systems have demonstrated good resistance to both water and SO_2 inhibition. Although the effects of SO_2 are not well known, recent investigations have suggested that the formation of sulfate on the silver surfaces actually improves the NO_x conversion of these catalysts (8-9). It is believed that the accumulation of sulfate on the silver sites increases the selectivity toward NO_x reduction, which correspondingly increases HC slip and reduces N_2O formation (9).

ETHANOL AS A REDUCTANT

Ethanol has been demonstrated to be a successful reducing agent for silver-doped alumina catalyst systems (1, 5, 8, 9). In the mid 1980s Caterpillar developed and marketed an ethanol-SCR system for use with stationary diesel engines; NO_x conversion efficiencies were around 75% (10). More recent studies have shown that when using ethanol as a reductant over alumina supported silver catalysts, NO_x conversion efficiencies greater than 90% were observed for a C1:NO_x ratio of 4 and a space velocity (SV) of 50000/h (10). In addition it appears that the NOx conversion efficiency is independent of the NO/NO_2 ratio (8-9). These investigations; however, were performed under controlled laboratory settings and actual performance data from engine tests are lacking.

Ethanol is also of interest because it can be easily incorporated into diesel fuel using an emulsifying agent. Ethanol has been evaluated as an additive to diesel fuel over the past 20 years to 1) lessen the demand for imported oil, 2) promote the use of a domestic renewable resource to power diesel engines, and 3) to lower particulate matter (PM) emissions. Previous efforts have shown that ethanol-diesel mixtures (commonly known as E-diesel) containing up to 15% ethanol are relatively stable and do not adversely affect engine operation (12).

RATIONALE OF CURRENT WORK

The primary rationale guiding this effort was to investigate the NO_x reduction potential for ethanol-SCR using a heavy-duty diesel engine. This included performing a convincing proof-of-concept for use of a fuel-borne reductant. Specifically, we wanted to show that the ethanol (contained within E-diesel) has the potential to reduce NO_x emissions via HC-SCR after being separated (by mild distillation) from the fuel blend and used as an injected reductant preceding an alumina supported silver catalyst. An on-board processing system (not part of this work) can be envisioned to strip ethanol from the base fuel and inject it into the exhaust as a reductant for NO_x conversion.

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NOMENCLATURE

C1	A means for expressing hydrocarbon concentration. It is obtained by multiplying the number of carbon atoms per molecule by the concentration in ppm.
DOE	Department of Energy
ECM	Electronic Control Module
E-diesel	A ethanol and diesel fuel mixture, usually containing a blending agent and mixed as a microemulsion
EGR	Exhaust Gas Recirculation
FG	Fuel Grade
FTIR	Fourier Transform Infrared
GC-MS	Gas Chromatigraph-Mass Spectrometer
HC	Hydrocarbon
HC-SCR	Hydrocarbon – Selective Catalytic Reduction
NO_x	Oxides of Nitrogen
NTRC	National Transportation Research Center
ORNL	Oak Ridge National Laboratory
PM	Particulate Matter
SCR	Selective Catalytic Reduction
SV	Space Velocity

MATERIALS AND EQUIPMENT

TEST FUELS

The test fuels investigated in this study included BP/ARCO ECD-1 and an E-diesel blend originally containing 15 vol.% ethanol, 1.5 vol.% blending agent, and 83.5 vol.% ECD-1. ECD-1 is a low sulfur diesel fuel (less than 15 ppmv) developed to reduce the levels of regulated emissions. The ethanol used in this study was fuel-grade (supplied by Williams-Pekin, Inc.) and is a corn-derived product denatured using gasoline and containing a corrosion inhibitor; pertinent specifications are listed in Table 1.

Table 1. Specifications for fuel-grade ethanol supplied by Williams-Pekin, Inc.

Ethanol content, vol.%	92.1 min
Methanol content, vol.%	0.5 max
Denaturant content, vol.%	2 min, 5 max
Water content, mass%	~0.5

The ethanol, ECD-1 fuel, and GE Betz additive (Blending Agent DMX10011) were splash-blended by Growmark Inc. at their manufacturing facility to form a stable micro-emulsion containing 15 % by volume ethanol.

REDUCTANTS

Fuel-borne reductant separation

Approximately 1 liter of ethanol was stripped from 7 liters of the E-diesel blend through the application of moderate heat and vacuum using a laboratory distillation device (Buchi RE-121 Rotovapor). Visual inspection showed that the distillate was of single phase. This suggests that the distillate was primarily ethanol since diesel fuel, including the light aromatic constituents, is immiscible with ethanol, even at low concentrations. This relatively simple test demonstrates the feasibility of using an on-vehicle device to remove lesser portions of ethanol from E-diesel.

The remaining ~6 liters of stripped E-diesel fuel (mostly depleted of ethanol) was added back to the original blend which subsequently lowered the ethanol content to ~13 vol.%. This partially stripped E-diesel was also evaluated as a test fuel.

Evaluated reductants

The two reductants evaluated in this study were fuel-grade ethanol in the as-received condition (untreated) and the ethanol portion that had been stripped (distilled) from the E-diesel blend. Both the untreated and stripped ethanol batches were evaluated as reducing agents while running the engine on ECD-1. Following these tests, the engine was operated using the 13 vol.% E-diesel blend while using the stripped ethanol as the reductant. A single test was performed using reagent-grade (high purity) ethanol.

SCR SYSTEM IMPLEMENTATION

The ethanol delivery system consisted of a cooled Buick gasoline injector, a fuel injection pump (Mallory Series 60FI), and a return style regulator, which was used to maintain pressure near 400 kPa. The injector was located in a bend in the exhaust 64 cm from the turbo outlet.

Caterpillar, Inc. provided two seven liter catalysts to ORNL. The catalysts had a cell density of 31 cells/cm^2 (200 cells/in^2) and measured 24.1cm (9.5 in) in diameter by 15.2 cm (6 in) long. They were installed in the exhaust at a distance of ~1.5 meters from the engine turbo outlet. During the initial test runs, the second brick was installed directly behind the first catalyst. During this investigation the exhaust was unfiltered (no particulate traps were used).

EXPERIMENTAL FACILITY

The evaluation was conducted at the National Transportation Research Center (NTRC) by ORNL staff. A Cummins 5.9 liter ISB turbo-charged, direct injection, diesel engine (1999 model, 24 valve, in-line 6 cylinder) was used as the test engine. This engine was altered from the commercially available version due to the addition of a Cummins supplied exhaust gas recirculation system and a non-standard ECM, fuel pump, fuel injectors, and turbine. The engine was rated for 175 HP and 2.5 g/HP-h of NO_x over the heavy-duty STP. The EGR valve could be controlled either via the ECM map or by manual override. The engine was coupled to a General Electric direct current motoring dynamometer capable of absorbing 224 kW (300 hp) and motoring 213 kW (285 hp).

The ethanol-SCR system layout and sample locations are shown schematically in Fig. 1. Gaseous emissions were sampled from the raw exhaust stream and directed to a standard emissions bench and a Fourier Transform Infrared (FTIR) spectrometer. The standard bench (composed of Horiba Ltd. and California Analytical Instruments analyzers) provided measurements of NO_x, THC, CO, CO_2, and O_2. The FTIR spectrometer (Nicolet Instrument Corp. Magna-IR 560) provided speciation of ammonia, N_2O, and acetaldehyde.

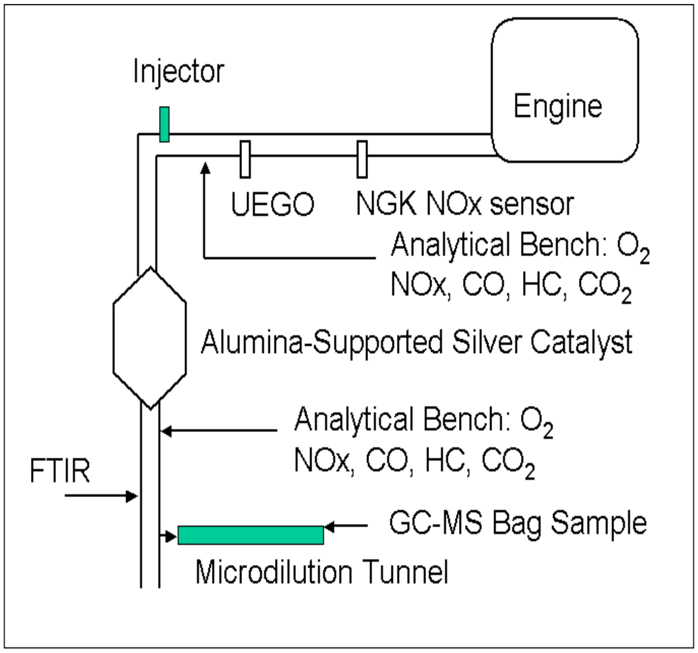

Fig. 1. Schematic diagram showing layout of ethanol-SCR components and sampling locations.

A stream of exhaust was sent to a micro-dilution tunnel for additional speciation via GC-MS and for measurement of N_2O and ethanol slip. Bag samples were drawn from the micro-diluter for hydrocarbon speciation via GC-MS. In addition a photoacoustic spectrometer (from Innova AirTech Instruments model 1312) was used to measure both ethanol slip and tailpipe N_2O emissions. This instrument has been used successfully to quantify ethanol emissions from vehicles operating on ethanol/gasoline blends (6).

Fuel consumption was measured using a Max Machinery Inc. fuel flow measurement system. Intake airflow was measured using a Marion laminar flow element. The space velocity of the gas flux was calculated and reported for standard conditions.

A custom PC-based system was used to control reductant injection. Injector duty cycle (% of time in open position) was adjusted to control the flow rate of ethanol into the exhaust. Other system parameters were held constant, such as the injector pulsing frequency (10 Hz) and the ethanol injection line pressure (~400 kPa) and ethanol temperature (30-40°C). The injection system was calibrated for a relevant duty cycle range using fuel-grade ethanol by injecting into a graduated cylinder for measured time periods.

EXPERIMENTS

INITIAL SHAKEDOWN AND CATALYST DEGREENING

Both catalysts were initially mounted in the exhaust. Initial shakedown evaluations were performed to evaluate the operation and performance of the ethanol delivery system, bench analyzers, and data acquisition system. The engine was run at several different operating modes for about 2 to 3 hours with reductant injection to briefly examine the performance of the catalysts in the green state. Following this, the catalysts were aged for approximately 10 hours while maintaining the engine exhaust temperature near 400°C.

REDUCTANT INJECTION

The general method for testing at a given condition (set engine speed and load, fuel type, reductant type, catalyst) was to begin with a relatively low reductant injection rate. After achieving steady-state conditions and recording data, the injection rate was increased. In this manner we would sweep across a reasonable range stoichiometry and stop when relatively high HC slip was observed.

SPACE VELOCITY COMPARISON

During the initial test results after aging we suspected that the first catalyst brick was providing the bulk of the SCR capability and that the second catalyst brick was relatively ineffective. For this reason, and also to achieve SV values in a realistic range, the downstream (or second) catalyst brick was removed. For most tests the ethanol-SCR system performance was evaluated for a relatively low SV of ~21000/h and a higher SV near 57000/h, while attempting to maintain the same narrow catalyst temperature range for both conditions. The engine operating modes corresponding to these two conditions are detailed below in Table 2. (SV is reported for STP.)

Table 2. Key engine operating parameters for space velocity evaluation

Space velocity (1/h)	Engine Speed (rpm)	Engine torque (ft-lbs)	Catalyst temperature (°C)	NO_x flux (g/min)
~21000	1115	230	350 to 380	1.5
~57000	2225	180	350 to 380	2.1

During normal operation the NO_x flux for the low-speed condition was significantly higher than the high-speed condition. The EGR valve was controlled to be partially open for the low speed (21000/h) condition in order to reduce the NO_x emissions. (During both operating modes the EGR valve is normally closed.) As revealed in the table, the NO_x flux ended up being higher for the high-speed condition.

TEMPERATURE EVALUATION

In addition to measuring the conversion efficiency of the catalyst between 350 to 400°C, data was also taken to evaluate performance between 250 and 350°C. The torque applied to the low-speed condition was reduced to obtain lower catalyst core temperatures. The conversion efficiency was evaluated for two C1(2X ethanol):NO_x ratios.

EVALUATION OF REDUCTANT AND FUEL TYPE

The performance of the SCR catalysts was determined as a function of the reductant type (untreated or distilled ethanol) for both the low and high-speed conditions while operating the engine using ECD-1 fuel. In addition the performance was also evaluated (for both conditions) using distilled ethanol as the reductant while operating the engine using the E-diesel blend (which was the source of the distilled ethanol). In order to gain insight into reductant impurity contributions, an additional experiment was performed utilizing high-purity reagent-grade ethanol with the engine operating on ECD-1 fuel. The NO_x flux and catalyst temperature did not change appreciably when running the engine on ECD-1 or E-diesel at the above two conditions. Bag samples for the GC-MS analysis were taken for several of the test sequences. Generally bag samples were taken for a perceived high and low slip condition (low and high reductant injection rates).

RESULTS AND DISCUSSION

DESCRIPTION OF TEST CONDITIONS

The test conditions depicted in Table 3 show the key operating parameters associated with each test condition, including the day each particular study was performed.

As shown in Table 3, we evaluated 8 conditions as part of this investigation. The test conditions labeled as 1, 3, 4, and 5 were repeated on later days. Key parameters included space velocity, fuel type, and reductant type.

ENGINE OPERATION AND EMISSIONS

Analysis of the engine-out emissions for both engine operating conditions is shown in Table 4. Both the chemiluminescent bench detectors and the FTIR spectrometer showed that the NO_x in the exhaust was primarily NO.

The engine-out NO_x emission levels were similar for both fuel types. However, the E-diesel fuel did produce a small increase in the emissions of HC and CO, which was consistent with earlier results when running the engine on this fuel type. There was also a drop in engine performance associated with E-diesel usage. This is expected since the energy density of the 13% ethanol fuel is about 6% lower than the straight ECD-1 fuel. In addition, the combustion characteristics for the two fuels are not identical.

NO_x CONVERSION RESULTS

The NO_x conversion efficiencies associated with the ethanol-SCR system were measured over a 2-week period in October 2002. The initial runs incorporated both catalyst bricks. However the back brick was removed since it lowered the SV to unrealistically low levels and made interpretation of the data more difficult. As shown in Figs 2 and 3 the NO_x conversion efficiency increased with increasing C1:NO_x ratio for both the low SV condition (Fig. 2) and the high SV condition (Fig. 3). The conversion efficiencies associated with the double brick installation are also included in the diagram, since this data represents the initial state of the catalysts following the de-greening period. (Note that because two catalyst bricks were used for this condition, the SV is one-half the value of the other presented data.) During the runs taken on October 8, 9, and 17 untreated fuel-grade (FG) ethanol was used as the reductant and the engine was operated using ECD-1 fuel. The engine was run using ECD-1 for the days of October 10 and 15, but distilled FG ethanol was used as the reducing agent for these evaluations. The Oct. 16 data was taken while running the engine on E-diesel and utilizing distilled FG ethanol as the reductant. This data set represents a simulation of a fuel-borne reductant, where the fuel used to run the engine was also used to supply the reducing agent for the catalyst. An additional data set taken on Oct. 17 using high purity reagent-grade ethanol is shown in Fig. 2.

Table 3. Operating parameters associated for each test condition

Test	date	Space Velocity	Fuel	EtOH Reductant
	shakedown tests		ECD-1	Fuel-grade, as received
	10 hrs, catalyst aging		ECD-1	none
1	Oct. 7, 8	10,500	ECD-1	Fuel-grade, as received
2	Oct. 8	28,500	ECD-1	Fuel-grade, as received
3	Oct. 8-10, 17	21,000	ECD-1	Fuel-grade, as received
4	Oct. 8, 15, 17	57,000	ECD-1	Fuel-grade, as received
5	Oct. 10, 15	21,000	ECD-1	Distilled from E-diesel
6	Oct. 16	21,000	E-diesel	Distilled from E-diesel
7	Oct. 16	57,000	E-diesel	Distilled from E-diesel
8	Oct. 17	21,000	ECD-1	Reagent grade

Table 4. Bench analyzer results for engine operating conditions and fuel type

Bench Results	1115 rpm/230 ft-lbs (21000/h)		2225 rpm/180 ft-lbs (57000/h)	
	ECD-1	E-Diesel	ECD-1	E-Diesel
NO_x, ppm	280-315	306-309	150-164	159-164
CO_2, %	10.1	10.1	7.4-7.7	7.1-7.3
HC, ppm	12-23	24-29	18-27	39-46
CO, ppm	253-320	213-216	107-135	170-172
Therm. Eff., %	38.1	36.0	31.6	29.7
BMEP, psig	95.5-97.5	97.4	73-76	75.5

The data presented in Figs. 2 and 3 show that NO_x conversion increased with increasing ethanol delivery (C1:NO_x ratio) for all operating conditions. These figures also show that the level of NO_x conversion increased with the progression of experimentation up to Oct 16 for both operating conditions. This effect did not appear to be influenced by either fuel or reductant type. For the low-speed condition (Fig. 2) the maximum level of NO_x conversion (associated with a C1:NO_x ratio of ~4) increased from ~70% (Oct. 7-8) to approximately 95% for the runs on Oct. 16 and 17. The higher SV condition presented in Fig 3 shows that the optimum C1:NO_x ratio increased to ~7.5 and the conversion efficiency increased from 74% (on Oct. 8) to around 85% for the Oct. 16 runs. This behavior is a strong indication that the catalysts had not been fully aged prior to evaluation. But, closeness of the data on Oct 16 and 17 suggests that catalyst aging was nearing completion on Oct. 16. The cumulative engine running time put on the catalyst prior to the Oct 16 runs was estimated to be around 32 hours. The degreening period that was used was based on input from catalyst chemists experienced with these catalyst systems. However, the exceptionally low fuel sulfur level of the ECD-1 fuel (<15 ppm) likely necessitated a longer aging period to ensure complete sulfate accumulation on the silver catalyst sites.

Because the catalyst performance improved with the sequence of experimentation, we had difficulty making detailed assessments of SCR performance with fuel type or reductant grade. However, the Oct. 17 data presented in Fig. 2 shows no observable difference in NO_x conversion performance when using either fuel-grade (untreated) or reagent-grade ethanol as the reducing species. Likewise, the Oct. 16 and 17 results shown in Fig. 3 indicate that NO_x conversion was not greatly affected when running the engine on E-diesel and using distilled ethanol as the reducing species.

The Oct. 16 results clearly demonstrate the utility of using ethanol as a fuel-borne reductant to reduce NO_x emissions. The NO_x conversion was over 90% for a C1:NO_x ratio of ~5 at 21000/h and near 85% for a C1:NO_x ratio of 7 at 57000/h.

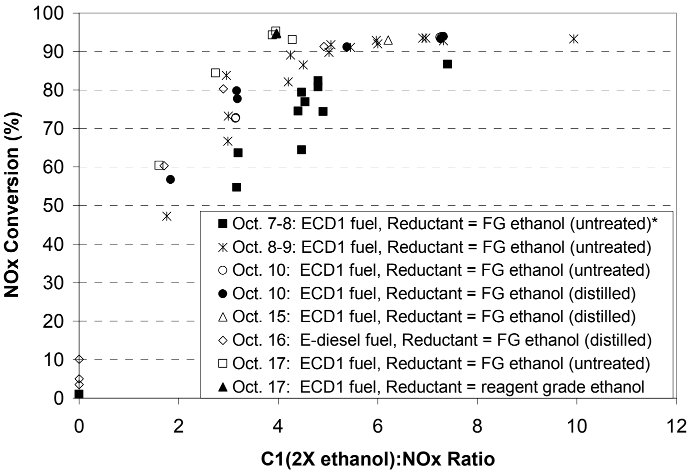

Fig 2. NO_x conversion as a function of C1:NO_x ratio for the low speed engine operating condition (1115 RPM, 230 ft-lb, ~21000/h space velocity. *Note, for this condition SV □ 10500/h.

FUEL PENALTY

For the experiments represented in Figs. 3 and 4, the C1:NO_x ratio can also be expressed as a fuel penalty. Figure 4 gives calculated fuel penalty on an energy basis as a function of the C1:NO_x ratio for the two engine conditions (Table 2.). It was assumed the ethanol reductant that is distilled from the fuel contains 63% of the energy on a weight basis compared to ECD1 fuel.

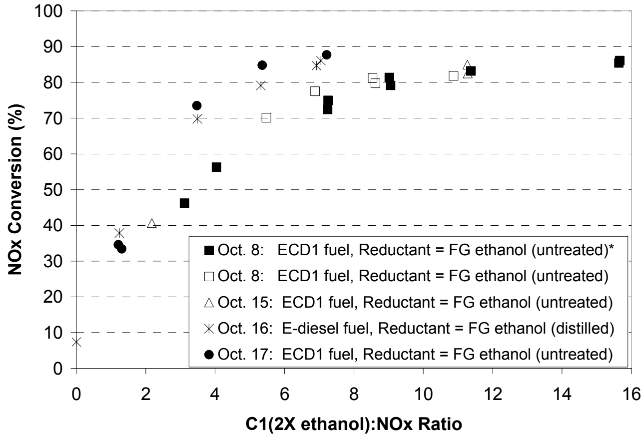

Fig 3. NO_x conversion as a function of C1:NO_x ratio for the high speed engine operating condition (2225 RPM, 182 ft-lb, ~57000/h space velocity. *Note, for this condition SV □26500/h.

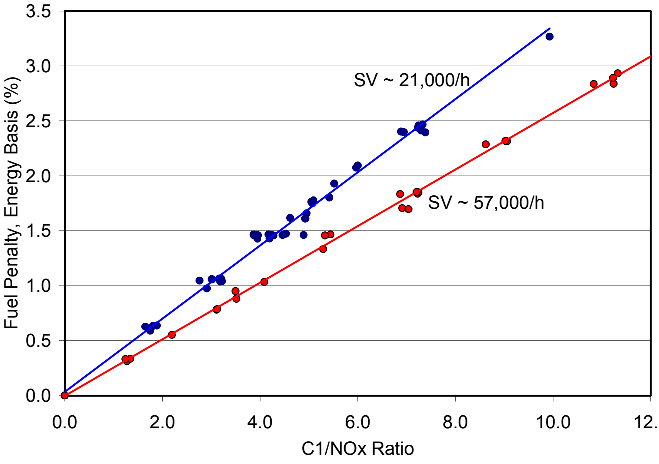

Fig 4. Fuel penalty versus C1:NO_x ratio for the two main engine conditions.

HYDROCARBON SLIP MEASUREMENTS

As shown in Table 2 the engine-out hydrocarbon emissions were low (< 50 ppm) for both operating conditions though there was a slight increase associated with using E-diesel as the fuel. These levels decreased further through the catalyst (when no reductant was added), thus indicating that some oxidation was taking place. However, the hydrocarbon emissions downstream of the catalyst increased with the addition of ethanol into the exhaust as depicted in Figs 5 and 6. (Note that the test conditions presented in Figs 5 and 6 correspond to those in Figs 2 and 3 respectively.)

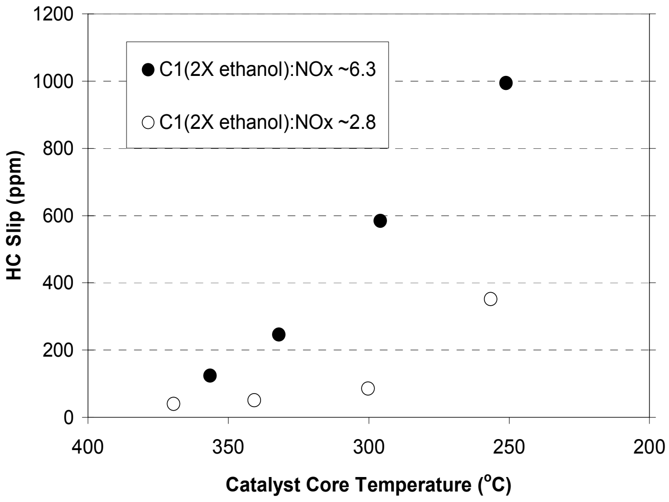

Fig 5. HC slip as a function of C1:NO$_x$ ratio for SV ~ 21000/h.

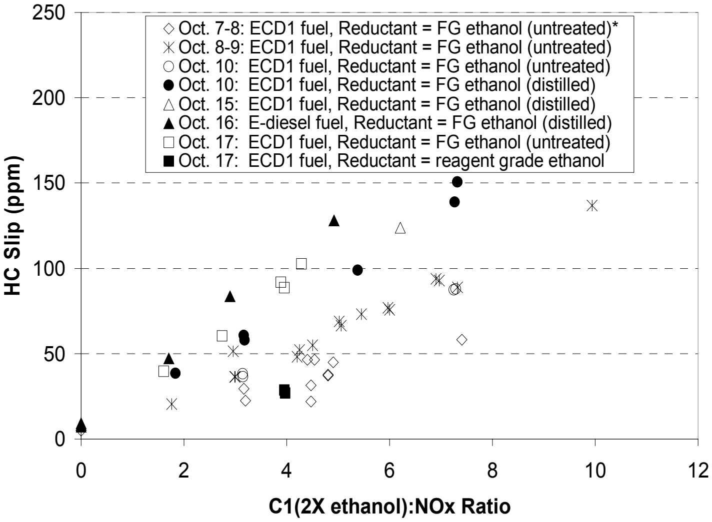

Fig 6. HC slip as a function of C1:NO$_x$ ratio for SV ~57000/h.

These figures also show that HC slip increased with succeeding experiments up to the runs on Oct 16. This further supports the assessment that the catalysts were insufficiently aged at the end of the de-greening period. These catalyst systems are believed to behave more like an oxidation catalyst in the green state; i.e. they oxidize HC species present in the exhaust. However, recent studies have indicated that as the silver sites become sulfated, these catalysts become more selective to NO$_x$ conversion, and hence their ability to oxidize hydrocarbons is reduced as the sulfate level increases (9).

During each test condition the HC emissions increase in an approximate linear manner with the flow rate of ethanol. As expected the slip was higher for the high-speed condition than the low-speed condition since the residence time is much lower. Assuming straight-line behavior, then for a C1:NO$_x$ ratio of 6, the HC slip is ~170 ppm for the high-speed condition versus ~150 ppm for the low-speed condition.

As with the data presented in Figs 2 and 5, the increase in slip associated with succession of experimentation prevents detailed assessment of HC slip. However, on Oct. 17 the HC slip was exceptionally low for the runs utilizing high purity reagent-grade ethanol as the reductant. This suggests that the impurities present in the fuel-grade ethanol may contribute substantially to HC slip (even if they do not influence NO$_x$ conversion).

TEMPERATURE EVALUATION

The conversion efficiency of this particular ethanol-SCR system is thought to be near optimum for catalyst temperatures near 400°C. However, during actual engine operation, the exhaust temperatures can be much lower, particularly during idling and low-load operation. Therefore we felt some measure of the low temperature performance of ethanol-SCR was needed. The results of this evaluation are shown in Fig. 7.

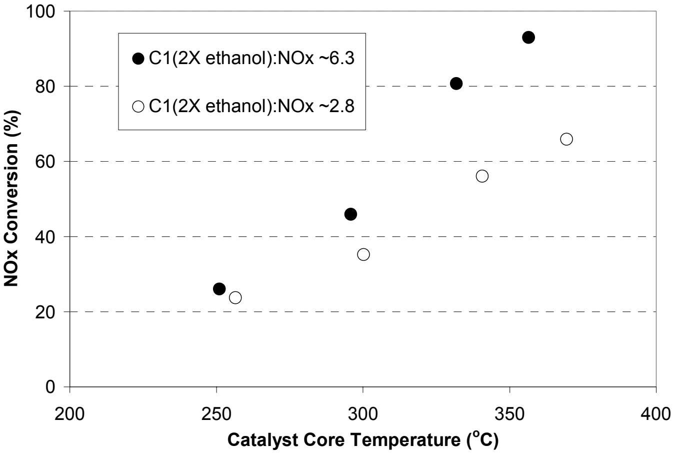

Fig 7. NO$_x$ conversion as a function of temperature.

Throughout this test, the engine was run at a fixed speed of 1115 RPM. The load was initially set to 230 ft-lbs to achieve a catalyst temperature between 350 and 400°C. Next, the load was gradually reduced to achieve temperatures approximating 350, 300, and 250°C. (Note that the SV dropped from 21000/h to 17000/h as the catalyst core approached 250°C.) The C1:NO$_x$ ratio was maintained near 6.3 and 2.8 for each temperature setting. The NO$_x$ conversion associated with these temperatures for both C1:NO$_x$ ratios is shown in Fig. 6.

The NO$_x$ conversion was observed to drop sharply with decreasing catalyst temperature for the two C1:NO$_x$ ratios studied. However, the two curves appear to converge near a value of ~25% as the catalyst temperature approaches 250°C. Without additional measurements it is unclear whether this value represents a lower bound. The hydrocarbon slip corresponding with the conditions presented in Fig. 7 are shown in Fig. 8. In this figure, the HC slip increases with decreasing catalyst temperature for both conditions. However the rise is much more dramatic for C1:NO$_x$ ratio of 6.3 versus 2.8. In fact the HC slip for the low C1:NO$_x$ ratio only begins to rise sharply when the catalyst core temperature is lowered to ~250°C. This suggests that the additional ethanol slips past the catalyst.

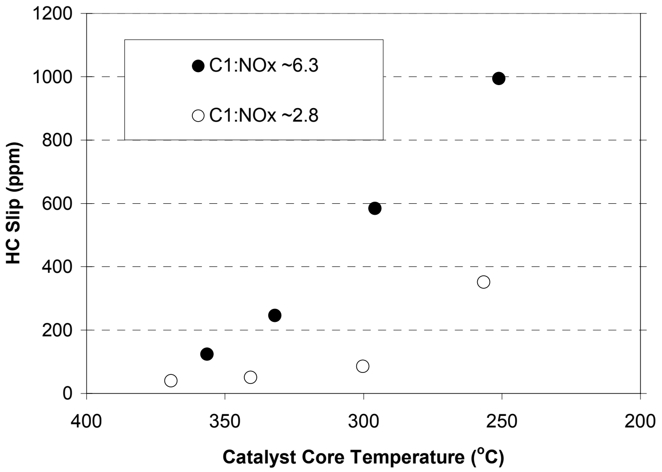

Fig 8. Hydrocarbon slip as a function of temperature.

FTIR RESULTS AND BAG ANALYSIS

FTIR Results

A Nicolet Magna-IR 560 FTIR spectrometer equipped with a REGA 700S sampling system was used to speciate NO_x, N_2O, ammonia, and acetaldehyde emissions from the catalyst exit as a function of SV and C1:NO_x ratio. The results for ammonia, N_2O, and acetaldehyde and their corresponding NO_x emissions are shown in Figs. 9, 10, and 11 respectively.

As shown in Fig. 9, ammonia was detected by the FTIR spectrometer and was observed to increase with increasing C1:NO_x ratio. Interestingly, the ammonia emissions were significantly higher for the low-speed condition than for the high-speed condition. This is an important finding since ammonia formation and its subsequent use to further aid in NO_x reduction is one of the pathways that is believed to occur for NO_x reduction by silver-loaded alumina catalysts (3). The lower residence time allows more ammonia to be formed, which subsequently may be important for the conversion of NO_x to N_2.

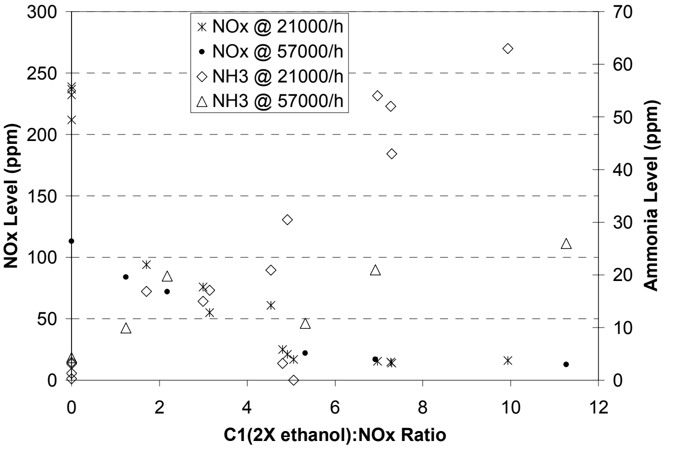

Fig 9. Ammonia emissions as a function of space velocity and C1:NO_x ratio.

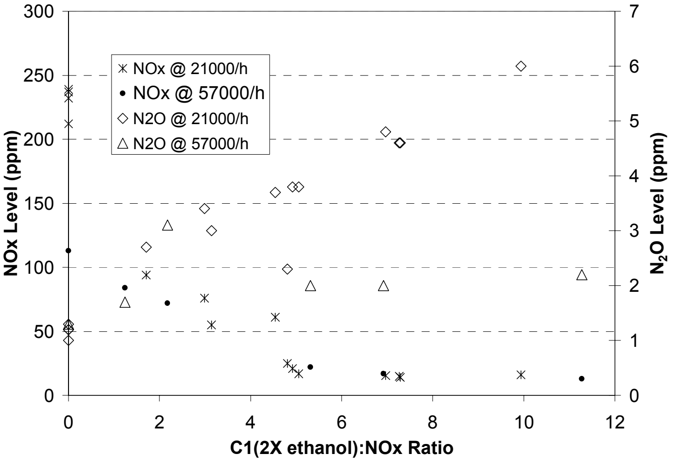

Fig 10. N_2O emissions as a function of space velocity and C1:NO_x ratio.

The N_2O emissions were also observed to increase with increasing C1:NO_x ratio (see Fig. 10); the concentrations of N_2O, however, are quite low (<10 ppm). This represents an important finding since early HC-SCR catalyst formulations emitted large concentrations of N_2O during NO_x conversion. Like the ammonia results, the N_2O emissions were higher for the low-speed condition indicating that residence time is critical for N_2O formation. The kinetics of N_2O formation and its role in NO_x reduction are not well understood.

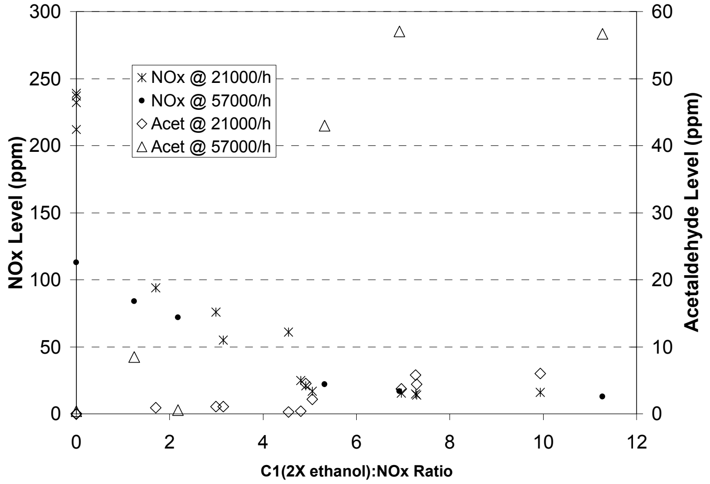

Fig 11. Acetaldehyde emissions as a function of space velocity and C1:NO_x ratio.

The emissions of acetaldehyde (shown in Fig. 11) were observed to increase with increasing C1:NO_x ratio and reached appreciable levels for the high-speed setting at moderate C1:NO_x ratios. Acetaldehyde emissions are formed directly from the oxidation of ethanol (via catalysis) and therefore would be expected to increase proportionally with ethanol concentration. The much higher acetaldehyde emissions associated with the high-speed condition suggests that 1) most if not all the ethanol is converted into acetaldehyde over the catalyst, and 2) the subsequent reactions utilizing acetaldehyde to reduce NO_x proceed less rapidly than does acetaldehyde formation. These results agree with the bench studies performed by Noto et al. (5) which showed that most of the ethanol is converted to acetaldehyde for these catalyst types.

Bag Analysis

The bag samples were collected using the miro-diluter highlighted in the Fig. 1 schematic. CG-MS analysis revealed that detectable levels of nitrophenol were formed during the ethanol-SCR process. Although we were not able to accurately quantify nitrophenol emissions, we are able to note that its concentration increased with ethanol delivery and space velocity.

CONCLUSIONS

A full-scale ethanol-SCR system demonstrated excellent reduction of NO_x emissions from a heavy-duty diesel engine for exhaust and catalyst temperatures of 350-400°C. The NO_x conversion reached 95% to 85% for space velocities of 21000/h and 57000/h respectively. In addition, the C1:NO_x ratios used to achieve these efficiencies were considered to be reasonable; approaching a value of 4 for 21000/h condition and around 7 for the 57000 condition. This represents energy based fuel penalties of approximately 1.5 and 1.8 % respectively. The NO_x conversion efficiency, however, depended greatly upon the catalyst core temperature. When the core temperature was lowered from ~360°C to ~250°C, the conversion efficiencies fell to near 25% for both speed conditions.

Because the catalysts were not thoroughly aged prior to testing, the NO_x conversion improved with progression of experimentation and thus interfered with data interpretation. The results suggest that the de-greening period needed to be extended to over 35 hours when using ECD-1 (and probably any low sulfur fuel) as the fuel type. The increase in NO_x conversion with succeeding experimentation was accompanied by an increase in HC slip which further supports the belief that the accumulation of sulfate on the silver catalyst sites actually enhances the NO_x conversion for these particular SCR systems.

This investigation also showed that the ethanol was rapidly converted to acetaldehyde by the silver-loaded alumina catalyst, which subsequently slipped past the catalyst at appreciable levels when the space velocity was increased to 57000/h. Ammonia and N_2O were also detected in the exhaust. The concentrations for both these compounds were observed to be higher for the low space velocity condition. However, the concentration of N_2O did not exceed 10 ppm, which is considered to be exceptionally low.

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