Hydrocarbon Selective Catalytic Reduction Using a Silver-Alumina Catalyst with Light Alcohols and Other Reductants

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ABSTRACT

Previously reported work with a full-scale ethanol-SCR system featuring a $Ag-Al_2O_3$ catalyst demonstrated that this particular system has potential to reduce NO_x emissions 80-90% for engine operating conditions that allow catalyst temperatures above 340°C. A concept explored was utilization of a fuel-borne reductant, in this case ethanol "stripped" from an ethanol-diesel micro-emulsion fuel. Increased tailpipe-out emissions of hydrocarbons, acetaldehyde and ammonia were measured, but very little N_2O was detected. In the current increment of work, a number of light alcohols and other hydrocarbons were used in experiments to map their performance with the same $Ag-Al_2O_3$ catalyst. These exploratory tests are aimed at identification of compounds or organic functional groups that could be candidates for fuel-borne reductants in a compression ignition fuel, or could be produced by some workable method of fuel reforming. A second important goal was to improve understanding of the possible reaction mechanisms and other phenomena that influence performance of this SCR system. Test results revealed that diesel engine exhaust NO_x emissions can be reduced by more than 80%, utilizing ethanol as the reductant for a space velocity near 50,000/h and catalyst temperatures between 330 and 490°C. Similar results were achieved for 1-propanol, 2-propanol and 1-butanol, with a (desirable) shift to a lower temperature range seen for the primary alcohols. Heavier alcohols and other oxygenated organics were also tested as reductants showing a range of less successful results. Non-oxygenated hydrocarbons and the selected secondary and tertiary alcohols proved to be very poor reductants for this system. Some discussion concerning the possible mechanisms behind the results is offered.

BACKGROUND

The use of hydrocarbons (HC) to reduce diesel exhaust NO_x emissions via selective catalytic reduction (SCR) is potentially a very attractive option for transportation applications. The exhaust stream is continuously oxygen rich under normal conditions and a ready supply of hydrocarbons is available on-board. However, the HC-SCR option is viewed by many to be less viable than lean NO_x traps and urea-based SCR technology. This view is not surprising: reported NO_x reduction efficiencies for HC-SCR systems are very often significantly lower than those achieved with these other technologies.[1-3] Alumina supported silver ($Ag-Al_2O_3$) catalysts are among the most promising of HC-SCR catalysts that have been examined in the open literature.[2,3]

There are numerous concerns with applying urea-based SCR and lean NO_x traps to on-road vehicles. For urea-SCR these include; 1) need for a separate onboard tank, 2) infrastructure to supply urea, 3) residue buildup from unwanted urea and urea decomposition products, especially during inadvertent over-injection or injection at low temperatures,[4,5] 4) corrosiveness of urea, and 5) cold weather freezing. Use of lean NO_x trap technology will require sophisticated controls to produce the needed frequency of calibrated fuel-rich pulses. Methods include various excursions in the engine operation, pulsed fuel injection into the exhaust stream, or both methods in combination. Occasional de-sulfurization of the lean NO_x trap requiring relatively severe conditions, will likely be necessary. The fuel penalty for effective lean NO_x traps may prove to be excessive and the required precious metal loading is a cost concern. All of the mentioned NO_x reduction technologies suffer from reduced effectiveness at lower temperatures (~150-300°C), which are typical for transportation applications.

Because of the drawbacks for urea SCR and lean NO_x traps, it would be attractive to develop a HC-SCR

system that could effectively utilize diesel (compression ignition) fuel, reformed diesel fuel, a fuel-borne additive or a reformed fuel additive as the reducing agent. As a result, investigators continue to pursue development of HC-SCR based systems with the hope of developing a viable technology.

SILVER-ALUMINA HC-SCR – SCR Catalysts utilizing HC reductants in oxygen-rich gas streams have been studied for at least two decades. There is a sizable body of literature relevant to HC-SCR and to $Ag-Al_2O_3$ catalysts in particular. Most published work has been bench-scale research using simulated exhaust. Two very notable, broad-based and complementary literature reviews were published in 2002, giving valuable interpretation to results reported by many researchers. One review was commissioned by the Coordinating Research Council,[2] to evaluate the state of SCR technology as applied to vehicles, and another was carried out by a team at Queen's University Belfast,[3] which looked closely at fundamental mechanisms. Of the great many HC-SCR systems evaluated, certain $Ag-Al_2O_3$ catalyst formulations have been identified as being particularly active and selective,[2,3] and therefore may yet be promising as a NO_x control technology for on-road diesel emissions.

Some generalization concerning $Ag-Al_2O_3$ catalyst performance can be made from the body of previous published research. Successful reducing agents include heavier paraffins, and certain alcohols and aldehydes. Catalyst formulations with 1.2% to 2% Ag are seen to lower the temperature at which alumina is active and selective.[2,3] Silver loadings near 10% can yield excessive levels of N_2O.[3] Some experiments resulted in conversion levels greater than 80% and demonstrated good resistance to both water and SO_2 inhibition,[2,3] qualities needed for diesel application. Sliver sulfate is active and resposible for good the performance reported (and low poisoning effect) with some reductants in the presence of SO_2.[3] In the presence of water, polar oxygenates seem to have quite an advantage. Inhibition by water is probably due to competitive adsorption (onto catalysts surfaces) between water and one or more key reactants. Highly polar oxygenates probably have a greater ability to compete with water in comparison to non-polar hydrocarbons.[2,3]

There are also significant hurdles to development of a robust $Ag-Al_2O_3$ system applicable to on-road diesels.[2,3] Diesel fuel and many components of diesel fuel do not appear to be good reductants, especially at relatively low temperatures (250-400°C). This leads to fuel-borne and fuel-derived/reformed reductants as a possible approach. Efficient use of reductants is also a likely issue, essentially a fuel penalty issue. To the best of our knowledge, the durability of $Ag-Al_2O_3$ catalysts for diesel applications remains unproven.

PREVIOUSLY REPORTED EFFORT - In a preceding study,[1] a full-scale $Ag-Al_2O_3$ catalyst ethanol-SCR system demonstrated excellent reduction of NO_x emissions from a heavy-duty diesel engine for a narrow range of conditions. For exhaust and catalyst temperatures of 350-400°C, NO_x conversion exceeded 90% and 80% for space velocities (SV) of 23,000/h and 62,000/h respectively. The C/N ratios used to achieve these efficiencies were about 4 for the 23,000/h SV condition and near 7 for the 62,000/h SV condition. As expected, the NO_x conversion efficiency was found to depend greatly upon the catalyst core temperature. When the catalyst temperature approached 250°C, the conversion efficiencies fell to near 25% for both SV values.

This previous study included a proof-of-principle demonstration of the fuel-borne reductant concept. A relatively simple laboratory method using "mild" vacuum distillation, was found to be quite effective for removing and collecting ethanol from E-diesel (ethanol-diesel micro-emulsion). Subsequently, this ethanol was used successfully as a reductant with the engine operation on an ethanol-diesel mixture.

The concept that ethanol is rapidly converted to acetaldehyde by the $Ag-Al_2O_3$ catalyst[2,6] was supported by the previous investigation.[1] Acetaldehyde was observed to slip past the catalyst at the 62,000/h SV. Ammonia was also produced in measurable quantities, and HC slip occurred. The addition of a "clean-up" catalyst that oxidizes or utilizes HC and NH_3 may be warranted for this type of system.

OBJECTIVE OF CURRENT WORK - A primary goal guiding this effort was to comparatively examine the effectiveness of various reductant candidates with the $Ag-Al_2O_3$ catalyst, under realistic engine conditions. It could be viewed as a (partial) reductant "screening" study for this particular catalyst. Interesting reductants or reductant "classes" could be examined in more comprehensive, follow-on studies. In a closer look at performance, the composition of slip HC and nitrogen compounds, and the feasibility of the reductant to be fuel-borne or fuel-derived would all be of great interest.

A second important goal was to increase understanding of chemical mechanisms and other physical processes governing the performance and selectivity of this HC-SCR system. Observing the relative performance of differing organic functional groups and other reductant properties values was expected to assist in gaining such understanding.

MATERIALS AND EQUIPMENT

EXPERIMENTAL FACILITY - The experimental effort was conducted at the Oak Ridge National Laboratory. A Cummins 5.9 liter ISB diesel engine (1999 model, 24 valve, in-line 6 cylinder) was used as the test engine. This engine is refitted to be a "near-2004" emissions engine, having unique controls/calibration, cooled exhaust gas recirculation (EGR), fuel system and turbocharger. Control of the EGR valve can be governed by the engine system or switched to

independent control. The engine was coupled to a General Electric direct current motoring dynamometer capable of absorbing 224 kW (300 hp).

The HC-SCR system layout and sample locations are shown schematically in Fig. 1. Gaseous emissions were sampled from the engine-out and catalyst-out raw exhaust streams and directed to standard emission benches (composed of Horiba Ltd. and California Analytical Instruments analyzers) to provide measurements of NO_x, THC, CO, CO_2, and O_2.
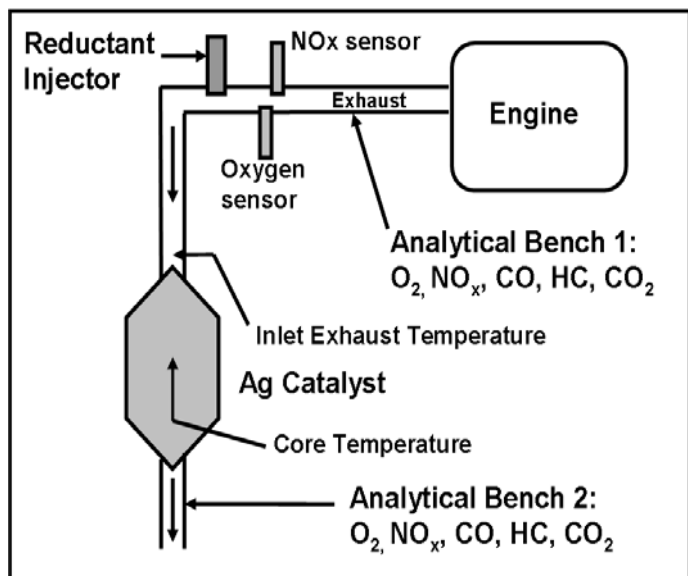

Fig. 1. Schematic diagram showing layout of HC-SCR components and sampling locations.

Caterpillar, Inc. provided the 7.0 liter $Ag-Al_2O_3$ catalyst to ORNL. The catalyst has 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. No other catalysts or particulate traps were used for this investigation. This catalyst was de-greened and tested for over 80 hours in the previous study.[1]

TEST FUELS AND REDUCTANTS - The fuels used to operate the engine were BP (formerly ARCO) ECD-1 and BP-15. Both are high cetane number, low sulfur diesel fuels (less than 15 ppm mass sulfur) and are viewed as very similar for the purposes of this study. The ethanol used in this study was fuel-grade (Williams-Pekin, Inc.), meaning it is denatured with gasoline and contains a corrosion inhibitor; pertinent specifications are listed in Table 1. The other reductants used in this work, listed in Table 2, were chemical-grade compounds, with the exception of 2-propanol which was 70% 2-propanol with 30% water.

Some reasoning behind the 13 reductants chosen for the test matrix is offered (upper portion of Table 2). The objective was to see if a trend existed going from lighter to heavier primary alcohols and how secondary and tertiary alcohols responded. The diols were chosen to see whether there was a benefit from a higher abundance of OH groups. This effect could be confounded because, in contrast to the alcohols, they are non-polar compounds with high boiling points. Cyclic compounds (Cyclohexane and cyclohexanol) were deemed interesting due to differing chemistry and their potential abundance in Canadian oil-sand derived fuels. An acetate and ketone were chosen to look at oxygenates with alternative functional groups. Admittedly, one could come up with a very different and longer list of compounds to test, with reasonable justification. The compounds listed in the lower portion of Table 2, were chosen mainly because they are fuels or fuel components.

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

Table 2. Reductants tested with $Ag-Al_2O_3$ catalyst.

Reductants used in 50,000/h SV test matrix		
Alcohols	**Molecular weight (amu)**	**Boiling Point or range (°C)**
fuel-grade ethanol	46.1	~ 79
1-propanol	60.1	97
2- propanol	60.1	82
1-butanol	74.1	117
tert-butanol	74.1	83
1-hexanol	102.2	157
cyclohexanol	100.2	67
1-octanol	130.2	196
ethylene glycol	62.1	196
1,3-propanediol	76.1	215
Other oxygenates		
ethyl acetate	88.1	77
acetone	58.1	56
hydrocarbon		
cyclohexane	84.2	81
Reductants used in miscellaneous tests		
low sulfur diesel fuel	C9-C20	185-350
low sulfur kerosene	Mostly C12-C15	175-325
iso-paraffin mixture		190-210
n-heptane	100.2	99

REDUCTANT INJECTION - The reductant delivery system featured a variable-speed dosing pump (Fluid Metering, Inc. model RHV 0CTC) to inject reductant into an entrainment air stream and then through a spray nozzle into the exhaust. The injector was located in a

bend in the exhaust about 1 meter from the catalyst face. An experiment was performed measuring reductant dispersion at the catalyst face while injecting a number 2 diesel fuel. The face of the catalyst was traversed in two perpendicular directions with a probe to obtain a concentration map. Results indicated nearly constant concentration for both a 28,000/h and 51,000/h SV condition. We have made the assumption that the (more volatile) reductants used in the current effort will also have essentially complete dispersion before reaching the catalyst face.

This injection system was calibrated by volume delivered as a function of pump motor speed. The system was thought to hold calibration reasonably well, even with changes in fluid (reductant) viscosity and modest changes in injection air pressure (the back-pressure seen by the pump). Calibrations were conducted at various times with water, diesel fuel, and ethanol and for varying entrainment air pressures (0 to 140 kPa above atmospheric pressure). The results support our assumption that the calibration remains valid with these changes. "Spot checks" of the calibration were performed periodically to be sure the system was working properly.

EXPERIMENTS

EXPERIMENT MATRIX - An experimental matrix was developed which would allow NO_x reduction performance comparisons of the various reductants over an applicable temperature range. A SV value of 50,000/h was chosen for most data because it is thought to be a broadly acceptable value for transportation applications.

The guidance for performing the experimental matrix for a given reductant is listed below.
- Space velocity: 50,000/h for most data; an optional test at 100,000/h to examine the role of SV.
- C/N range of at least 0 to 10, vary range as applicable. Collect data at several C/N values to define a meaningful curve.
- Engine out NOx concentration near 200 to 240 ppm
- Catalyst inlet temperature range, 250°C to highest achievable with the engine system, ~450-470°C. Examine at least 5 temperatures in this range.

It was found in practice to be difficult to keep the NO_x concentration at a constant value over the range of temperatures (and at 50,000/h SV) but it could be kept within a 200-240 ppm range by adjusting the speed, load, and EGR valve position.

The usual method for testing at a given exhaust condition and reductant type, was to begin with no injection and to progress in discrete steps from a low to high injection rate. Data was recorded at a given injection rate when a steady-state condition was observed. The data acquisition system was programmed to give real-time traces of temperatures,

NO_x and HC concentrations and other values, so progression to an apparent steady state could be observed more easily. In this manner a sweep across a reasonable range of stoichiometry was performed.

Typical test conditions used for an individual reductant are given in Table 3. The gas concentrations are representative values, given to show how the exhaust environment changes with test condition. The presence and concentration of O_2 and H_2O may change the behavior of the HC-SCR system somewhat.[2,3,6] Note that the catalyst is also exposed to particulate matter (PM), but no measurements of PM were made in this work. In some cases points between those listed for conditions 1-5 were also explored to obtain some data at other temperatures. Condition 6 was not run for every combination.

Table 3. Approximate test conditions used to explore reductant performance.

Test Condi-tion	SV (1/h)	Catalyst inlet Temperature (°C)	O_2 conc. (%)	CO_2 conc. (%)	H_2O conc. (%)
1	50K	260	13.2	4.8	6.5
2	50K	295	12.3	5.4	7.1
3	50K	335	10.6	6.5	8.2
4	50K	390	8.5	7.8	9.6
5	50K	465	5.5	9.8	11.9
6	100K	380	10.5	6.5	8.2

SEPARATION OF FUEL-BORNE REDUCTANTS - A very limited number of tests have been performed examining how effectively reductants mixed with diesel fuel could be removed using a laboratory "mild" vacuum distillation method. If the laboratory method worked well, it would at least be imply that an on-board device could be developed to carry out this function. Results show that light alcohols are easily removed by this method. More details of these tests are given in the Appendix.

RESULTS AND DISCUSSION

The majority of results presented focus on NO_x conversion as a function of catalyst core temperature for reductant injection at a given C/N ratio. Data taken for reductant injection at relatively high C/N values is presented first. The objective is to compare reductant effectiveness and identify those that demonstrate good performance. A more in-depth examination of selected reductants at a range of C/N values is offered as well.

GENERAL REDUCTANT SCREENING - The result of a test matrix using ethanol as the reductant is shown in Fig 2. The best performance is seen at the 388°C catalyst inlet exhaust condition. All results are at the 50,000/h SV condition unless noted otherwise. This

figure depicts the type of data set produced for each reductant tested.

Overall results in the form of NO_x reduction versus the catalyst core temperature are given in Figs 3-6, for C/N values of 9-12. The available data with C/N values nearest the middle of this range (10.5) were chosen for subsequent figures. Variation in the C/N values is due to the practicalities of engine operation and reductant injection. The range of C/N ratios vary from about 9-12, with some variation point to point for a given reductant and variation between reductants. This would be quite problematic, but this relatively high level of reductant injection, only small changes in performance occur over C/N values of 9 to 12, as seen in fig. 2. This "diminishing
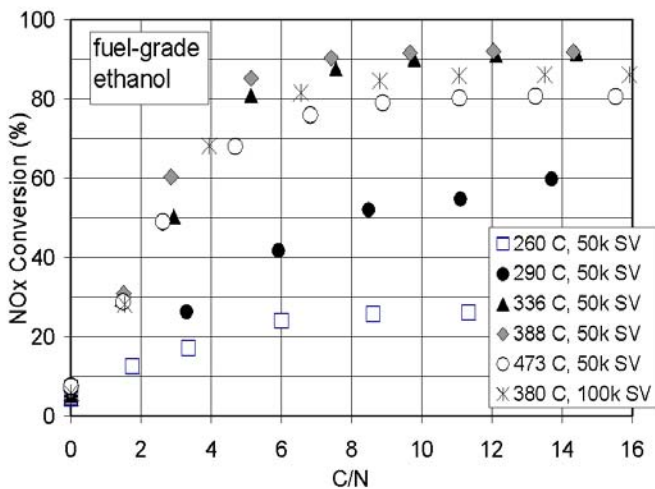
Fig. 2. Performance of fuel-grade ethanol for 50,000/h SV and five catalyst inlet temperatures. A 100,000/h SV case is included for comparison.

returns" observation held true for all reductants with the exception of ethylene glycol, which behaved rather linearly in this range (but showed this diminishing returns trend for C/N ≥ 20). The C/N ratio variation adds some uncertainty to the comparisons, but we believe the data is still highly useful in this form to compare relative performance of the reductants. Interpolated data is used for the ethylene glycol curve (fig. 5), which was missing some data points in the 9-12 C/N range and behaved more linearly over this range. A C/N value of 10.5 was chosen to be plotted. Catalyst core temperature is measured by a small thermocouple in a central channel near the geometric center of the monolith.

Selected light alcohols - We found the most effective reductants tested are the light alcohols, as depicted in Fig. 3. 1-Propanol and 1-butanol both show a desirable shift toward effective NO_x reduction at lower temperatures. It appears that 2-propanol is slightly less effective than 1-propanol and butanol. Because of the body of data generated in the previous study,[1] ethanol is a "base case" reductant and included in Figs. 4-6, along with 1-propanol which gave very favorable results.

Other alcohols - Performance results for 1-hexanol, 1-octanol, tert-butanol and cyclohexanol are given in Fig. 4. The heavier primary alcohols show significantly less NO_x reduction compared to the lighter alcohols, except at temperatures nearing 250°C where performance appears to be about the same. Both tert-butanol and cyclohexanol appear to have no value as a reductant with this catalyst.
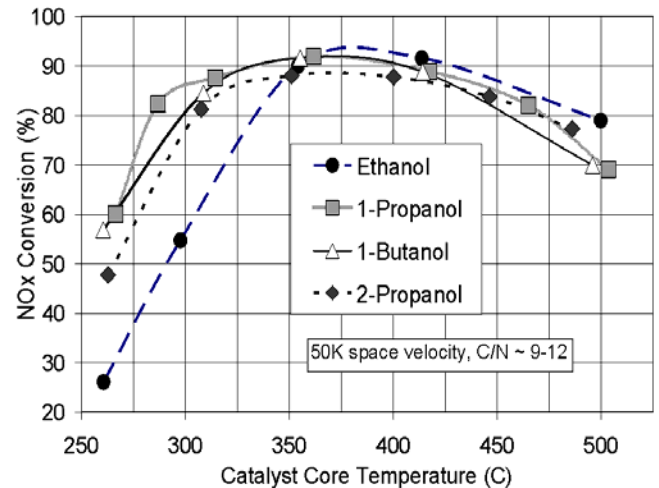

Fig. 3. Performance of light alcohols for 50,000/h SV and relatively high C/N ratio (reductant injection rate).
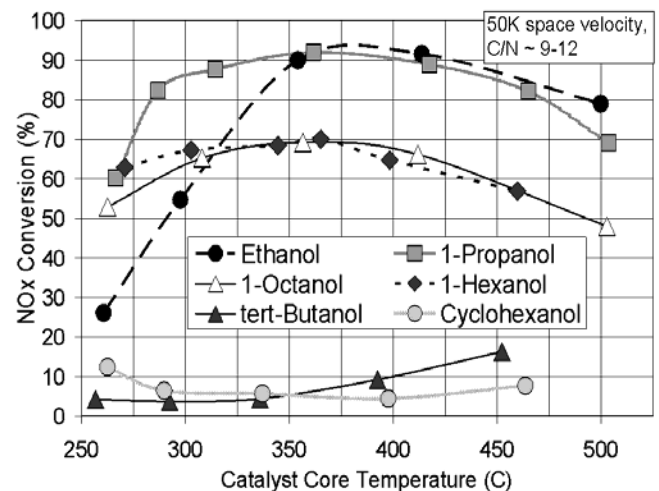

Fig. 4. Performance of 1-hexanol, 1-octanol, tert-butanol and cyclohexanol compared to ethanol and 1-propanol for 50,000/h SV and relatively high C/N ratio.

Diols - Results for two diols, 1,3-propanediol and ethylene glycol are summarized in Fig. 5. The 1,3-propanediol is seen to be moderately less effective as a reductant compared to the light alcohols, although it performs as well or better than ethanol at 250-300°C. Ethylene glycol appears similar to ethanol and 1,3-propanediol at 275°C, but is much less useful above 300°C.

Other non-alcohols - Figure 6 shows test results for the non-alcohol oxygenates, ethyl acetate and acetone,

which seem to work relatively well as reductants near 400°C and above. Also shown is a non-oxygenate, cyclohexane, which displays essentially no reductant capability with the tested system.
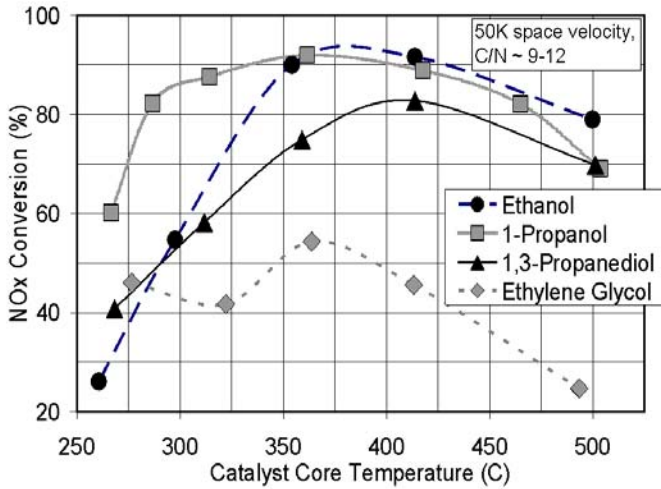

Fig. 5. Performance of diols compared to ethanol and 1-propanol for 50,000/h SV and relatively high C/N ratio. The ethylene glycol data is interpolated to give results for C/N = 10.5.
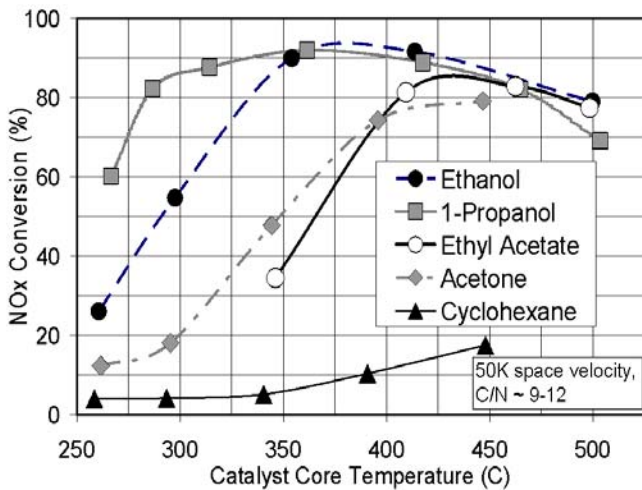

Fig. 6. Performance of ethyl acetate and acetone does not compare well to light alcohols, especially at the lower end of the temperature range. Cyclohexane shows little activity as a reductant.

EXAMINATION OF LIGHT ALCOHOL INTERPOLATED RESULTS - The results for the light alcohols will now be examined in more detail. Plots of performance at C/N values of 3.0, 6.0 and 9.0 were produced by interpolation of the raw experimental data. Results for ethanol, butanol and propanol are shown in figs. 7, 8 and 9. Diminishing returns of increased reductant injection going from a C/N value of 6 to 9 is evident, particularly for the ethanol injection. Comparisons of the four alcohols at C/N values of 3, 6 and 9 are shown in figs. 10, 11 and 12

A few observations can be made from figs. 7-12. Ethanol shows only marginal improvement in NO_x performance when C/N is increased from 6 to 9. For temperatures near 350°C and above, ethanol is the best reductant, especially for C/N of 3 and 6. 1-propanol and 1-butanol are clearly better at lower temperatures over the range of C/N values.
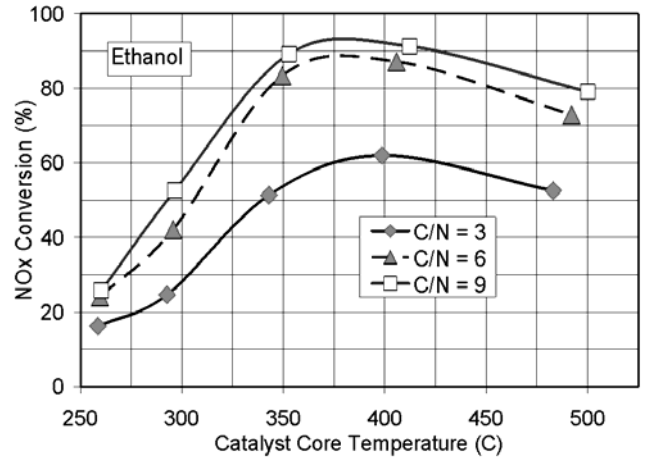

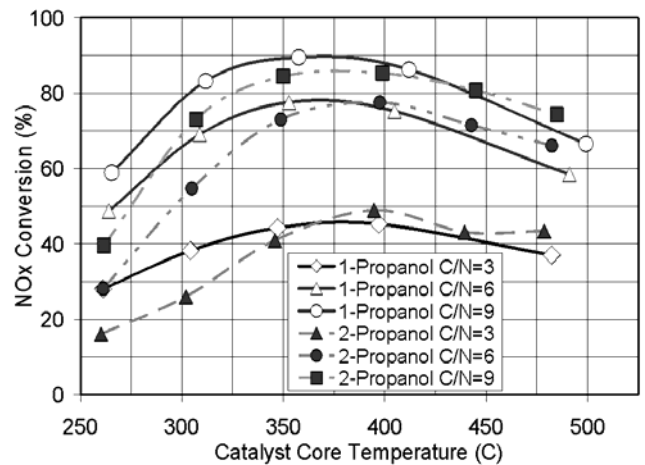Fig. 7. Interpolated data for ethanol experiments.

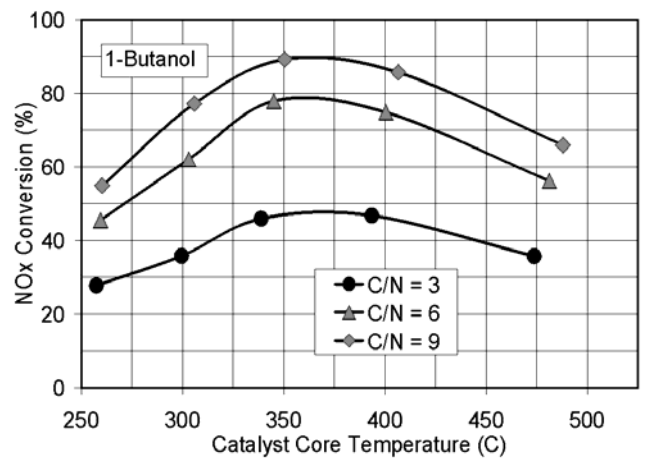Fig. 8. Interpolated data for 1-propanol and 2-propanol experiments.

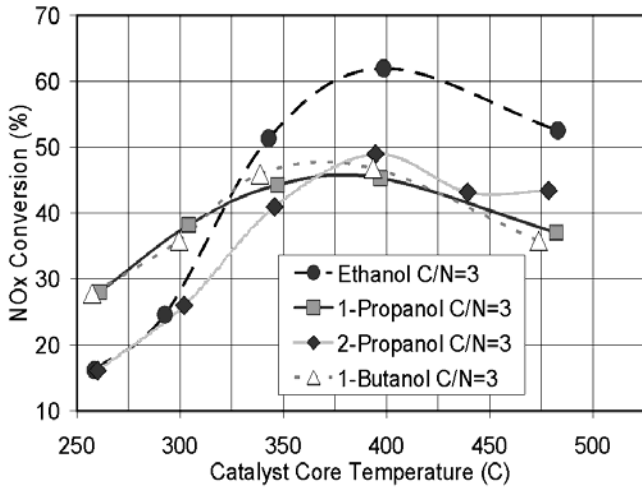Fig. 9. Interpolated data for 1-butanol experiments.

Fig. 10. Comparison of light alcohols for C/N = 3.0 from interpolation of data.
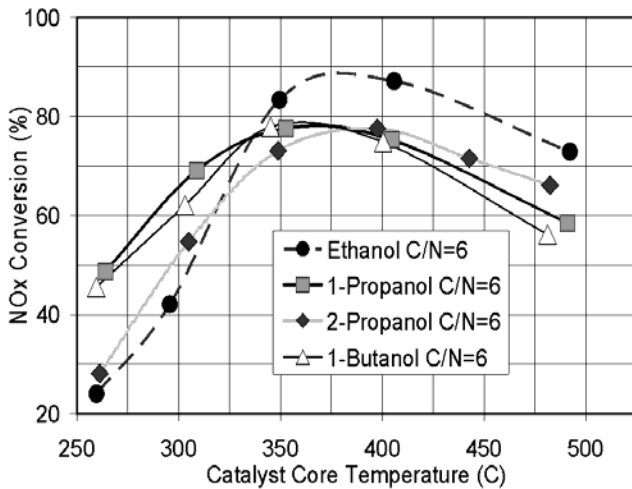

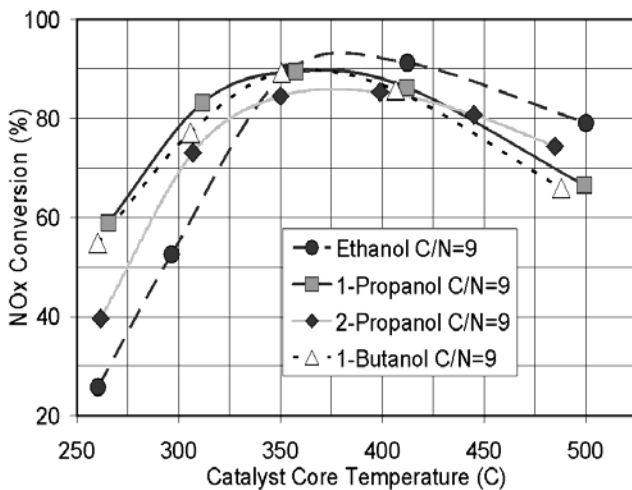Fig. 11. Comparison of light alcohols for C/N = 6.0 from interpolation of data.

Fig. 12. Comparison of light alcohols for C/N = 9.0 from interpolation of data.

OTHER RELATED EXPERIMENTAL EFFORTS – Some data is available from separate, but related efforts using the same HC-SCR system. The major practical difference is the SV and NO_x levels were not held at 50,000/h and 200-240 ppm values used for the main body of data. Results for a low sulfur number 2 diesel fuel, a low sulfur kerosene, an iso-paraffin mixture and fuel grade ethanol are compared in Fig. 13. The compounds other than ethanol are rather ineffective as reductants. A single test using heptane at 100,000/h SV and 350°C exhaust temperature (not shown) gave only a few percent NO_x conversion. Considering the cyclohexane results discussed earlier, the non-oxygenated reductants tested in this study all gave poor results. These potential reductants were alkanes or contained a large amount of alkanes compounds, and other types of non-oxygenates may give different results.
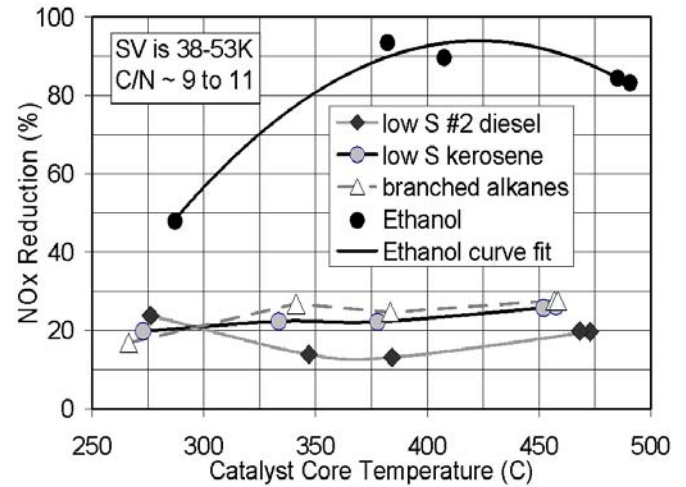

Fig. 13. Data comparing fuel-grade ethanol to relatively heavy hydrocarbon reductants.

FUEL PENALTY FOR ETHANOL USE – Fuel penalty is often defined as the reductant consumption rate divided by the engine fuel consumption rate, and can be expressed in percent by mass or energy units. Fuel penalty might be stated for a given engine condition or some standard engine test cycle. We offer fuel penalty values for injecting ethanol as the reductant in Table 4, for the six tested engine conditions used in this study (Table 3).

Table 4. Fuel penalty for ethanol injection for a 200 ppmv exhaust NOx concentration and a 10:1 C/N ratio.

Test Condi-tion	Engine power (kW)	Fuel consump-tion (g/s)	BMEP (kPa)	Ethanol Mass Penalty (%)	Ethanol Energy Penalty (%)
1	36	2.85	345	6.4	4.0
2	44	3.23	452	5.7	3.6
3	58	3.89	631	4.7	3.0
4	73	4.70	827	3.9	2.5
5	94	5.90	1186	3.1	2.0
6	95	6.92	841	5.3	3.3

DISCUSSION OF REDUCTANT PERFORMANCE – Some explanations and conjecture can be offered addressing the hierarchy in performance among reductants tested.

Aldehyde formation - There is experimental evidence that ethanol, and 1-propanol undergo oxidation to form acetaldehyde and propionaldehyde[1,6] and it is then likely that 1-butanol also forms the corresponding aldehyde. The aldehydes, which are also good reductants, break down further as part of the reduction process.[1,6,7] It is proposed that 2-propanol forms acetone[6] which then breaks down further. We note that 2-propanol was quite superior as a reductant compared to acetone, especially at low temperatures, so this explanation may not be fully satisfactory. In forming either an aldehydes or ketone, the alcohol donates two H atoms, which presumably enhance in the overall reduction process. Tert-butanol would not be expected to form an aldehyde or a ketone and proved to be relatively unreactive for the tested system.

Reactivity - A general (and perhaps obvious) observation can be made based on molecular stability, simply that reductants that react or break down easily are likely to create "usable" reactive species, particularly at low temperatures. This might explain ethyl acetate and acetone looking like reasonable reductants at ~ 400°C, but not at low temperature, where they remain relatively stable. There was some expectation that the cyclohexanol would have reactivity, and behave somewhat like hexanol or a secondary alcohol. Instead, cyclohexanol appeared stable and unreactive with the tested system.

Reactivity indications - Evidence of the (net) oxidation of reductants can be inferred from the measured CO_2, CO and HC levels and the temperature difference between the catalyst inlet and the catalyst core. The net reactions occurring appear to be quite exothermic. Unfortunately the CO_2 measurement is dominated by the engine-out values (~5-10%) and the increase derived from the reductants is about 0-2500 ppm in the range of interest. Furthermore the flame ionization detector for HC measurement used in this work gives useful information, but has a response that varies widely for many of the species likely being detected, and the actual HC slip species are not necessarily known. It is not possible to compare and interpret the CO_2 and HC readings with confidence. However, a rise in CO and CO_2 is expected for the compounds that decompose and oxidize along with a relatively low HC reading, and the opposing trends are expected for compounds that are unreactive.

Analysis of the CO_2 "rise" data for he C/N values of 9-12 examined earlier, gave somewhat crude and scattered results, but we report a few trends that were seen. The poorest performing compounds, cyclohexane, cyclohexanol and tert-butanol, showed virtually no detectable CO and CO_2 formation except at the highest temperature condition (see Table 3.) where it is estimated 15-30% of the injected carbon ended up as CO and CO_2. These compounds also gave consistent and high HC readings (accounting for ~68-87% of the injected carbon, depending on the reductant) for the lower temperature conditions (conditions 1-4 in Table 3) with a modest drop in HC value for the highest temperature condition (condition 5 in Table 3). Cyclohexanol was only observed to decompose at the highest temperature point, and when a high injection rate was held for about 15 minutes as the catalyst temperature rose from 477 to 495°C. Measured CO_2 increased and HC reading decreased as might be expected. All other reductants gave much higher values for CO + CO_2 production, with increasing values for increasing temperature, and the opposing trend for the HC emissions. Ethylene glycol stood out as having the highest propensity to react to form CO + CO_2, at all temperatures (~ 80 % at the lowest temperature, and rising to ~ 100% at the highest temperature), followed by 1,3-propandiol and ethyl acetate. Ethylene glycol also displayed the highest degree of exothermic activity for the low temperature tests.

Polar compounds, water solubility - It has been proposed that a distinct advantage is possessed by the more polar oxygenates which can compete successfully with water for adsorption sites.[2,3] The environment of interest has abundant water which doubtlessly affects the catalytic process. This property again favors the light alcohols and light asymmetric oxygenates. Note that the non-polar diols tested do have very high water-solubility, and may be less disadvantaged compared to low water-solubility compounds. Hexanol and octanol notably have lower water solubility than the lighter alcohols. The non-oxygenated compounds have very low solubility.

Molecular mobility - The ability of the compound to diffuse to make intimate contact with the catalyst surface and then be mobile on the surface, could affect the SCR process. This mobility property could be related to the molecular weight, boiling point (listed in Table 2) and other properties of the compound. No attempt to quantify this concept or property is offered. Indirect evidence of some sort of physical interference process, probably involving carbonizing (coking) of the reductant on the catalyst surface, was seen with octanol and compounds of higher molecular weight. The observation was that as spray injection quantity was increased, NO_x conversion began to decrease and would then slowly decrease with time at a given spray rate.

LOW TEMPERATURE PERFORMANCE - A key technical challenge for lean NO_x trap and SCR systems applied to diesel transportation is effectiveness at low catalyst temperatures; the 150-300°C range will serve for the purpose of this discussion. The Ag-Al$_2$O$_3$ SCR system will need to have reasonable effectiveness in this temperature range to have viability for on-road applications for the 2007-2010+ emission requirements.

The tested system did show > 50% NO_x reduction at 260-270°C for 1-propanol, 1-butanol, 1-hexanol, 1-octanol for C/N of 9 or below as shown in Fig. 14. Fig 3. results imply that 1-propanol and 1-butanol will have a steep performance drop as the temperature is dropped below the range of the data presented. Hexanol is particularly interesting because it shows the best performance in fig. 14, and from fig. 4 seems to be in a "shallow" rather than steep decent as temperature drops toward 250 C and beyond. This latter trend is also true for octanol (fig. 4). Greater than 50% NO_x reduction could also be achieved with ethylene glycol at C/N ratios greater than 12. Better understanding of the mechanisms governing the Ag-Al$_2$O$_3$ SCR system at temperatures below 300°C could prove highly valuable in knowing if and how this type of catalyst can be significantly improved upon. Perhaps future tests should target the lower temperature range.
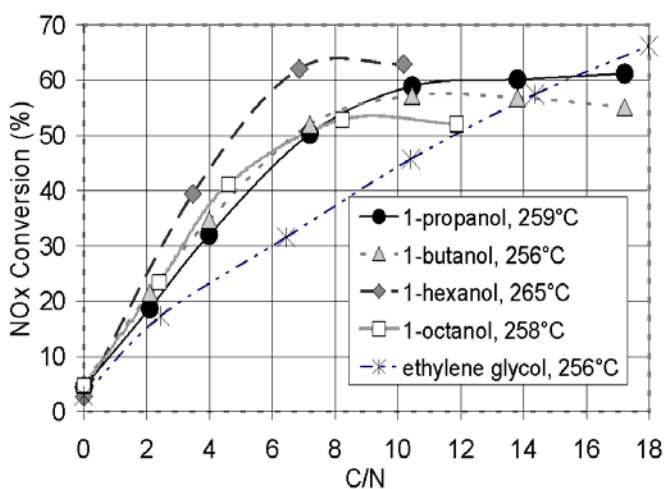

Fig. 14. Low temperature performance results for the five "best" low temperature reductants.

CONCLUSIONS

The tested HC-SCR system performed well with ethanol, 1-propanol, 2-propanol and 1-butanol as reductants over the range of conditions explored. These light alcohols gave greater than 80% NO_x reduction over a broad temperature range for C/N of 9 or greater and 50,000/h SV. A desirable shift toward effective NO_x reduction at 260-300°C, was seen for 1-propanol, and 1-butanol. Relatively good performance in the 260-300°C temperature range was also found for 1-hexanol and 1-octanol, but with reduced performance at higher temperatures compared to the lighter alcohols. A significant challenge for diesel NO_x aftertreatment systems is effectiveness at catalyst temperatures, of 150-300°C. The tested system gave > 50% NO_x reduction at 260-270°C for number of primary alcohols (1-propanol, 1-butanol, 1-hexanol, 1-octanol) for a C/N ratio of 9 or below.

Potential reductant candidates that performed quite poorly include tert-butanol, cyclohexanol, cyclohexane, n-heptane, number 2 diesel fuel, kerosene and an iso-paraffin mixture.

1,3-propanediol is seen to be somewhat less effective as a reductant compared to the light alcohols, although it performs as well or better than ethanol at 250-300°C. Ethylene glycol also performed comparatively well at low temperatures, but is a relatively poor reductant at 300°C and beyond.

Other tested oxygenates were ethyl acetate, and acetone. Both are seen to be good reductant at 400°C and above but not at lower temperatures.

Some overall patterns were observed from the testing of the 17 reductants with this particular SCR system. The results can be associated with certain chemical and physical properties of the reductants tested. Highly polar (and water soluble) compounds are thought to have a significant advantage, because they compete successfully with water for catalyst surface sites. Low molecular weight may be advantageous, allowing high diffusion rates and/or good surface mobility. High chemical reactivity in the appropriate temperature range is also desired. This explains the superior performance of light alcohols (ethanol, 1-propanol, 2-propanol, butanol), which have the previously mentioned attributes. Furthermore, the primary alcohols appear to be very reactive, readily forming aldehydes while donating two protons (which are assumed to help drive reduction) per molecule in the process. In an analogous fashion, 2-propanol likely forms a corresponding ketone with the same desirable proton donation.

These concepts can be applied to the other reductants. The heavier primary alcohols tested, 1-hexanol and 1-octanol, did not perform as well as the lighter alcohols, probably due to being incrementally less polar and mobile. The diols tested were symmetric and non-polar, but appeared to be reactive. Testing a 3 or 4 carbon (non-symmetric) polar diol could shed more light on these contentions. Ethylene glycol stood out as being exceptionally reactive toward oxidation but was relatively poor at selective reduction of NO_x. This appeared to be true for 1,3-propandiol but to a much lesser extent. The other tested alcohols, tert-butanol and cyclohexanol were quite unreactive with the catalyst used.

For the non-alcohol reductants we see that the oxygenates, ethyl acetate and acetone, are low molecular weight and polar, but are not reactive at lower temperatures. The non-oxygenated compounds are not water soluble, and probably have some difficulty competing well for active surface sites. The relatively long-chain hydrocarbons showed more reactivity than n-heptane or cyclohexane, a general trend also seen in the literature.

More could be learned by examining the HC and nitrogen containing slip species and or those found at different positions within the catalyst through in-catalysts

sampling. A follow-on effort of this type for selected reductants may be considered.

Another question to investigate is the feasibility of the successful reductants to be fuel-borne or fuel derived. Ethanol/diesel mixtures have been examined due to abundant and relatively inexpensive domestic ethanol production. Such fuel has several drawbacks including flammability/safety issues. More could be done to look into what other alcohols are feasible as either fuel-borne removable reductants, or that could be produced on-board from diesel fuel or a fuel-borne additives.

ACKNOWLEDGMENTS

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

amu	atomic mass units
$Ag-Al_2O_3$	Catalyst composition of silver on an alumina substrate
C/N	Atomic ratio of carbon in the reductant to nitrogen in NO_x
E-diesel	A ethanol and diesel fuel mixture, usually containing a blending agent and mixed as a microemulsion
EGR	Exhaust Gas Recirculation
FTIR	Fourier Transform Infrared
HC	Hydrocarbon
HC-SCR	Hydrocarbon – Selective Catalytic Reduction
k	thousands
NO_x	Oxides of Nitrogen
NTRC	National Transportation Research Center
ORNL	Oak Ridge National Laboratory
PM	Particulate Matter
ppmv	parts per million by volume
SCR	Selective Catalytic Reduction
SV	Space Velocity referenced to 25 °C, units

APPENDIX

A very limited number of tests were performed examining how effectively reductants mixed with diesel fuel could be removed using a laboratory "mild" distillation method. The distillation conditions were 90°C, 27 kPa vacuum.

It is seen that ethanol, 1-propanol and 1-butanol can be removed by this method. As might be expected, octanol

with a boiling point of 196°C, was not recoverable. Hexane and heptane were partially recoverable.

Table A1. Results of mild distillation testing.

Fuel Additive	boiling Point (°C)	Mole-cular weight (amu)	Amount blended into ECD1 fuel (%)	Amount recovered by mild distillation (%)
Fuel-grade ethanol	~ 79	46.1	20	20
1-propanol	97	60.1	20	18
1-butanol	117	74.1	20	17.5
n-hexane	69	86.2	20	5
n-heptane	98	100.2	20	5
1-octanol	196	130.2	20	0