Abstracts

SESSION 11 – Emission Control/NO_x Reduction

Chair: **Ron Graves, Oak Ridge National Laboratory**

Diesel Emission Control Technology in Review

Tim Johnson
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This presentation will review the field of Diesel emission control with the intent of highlighting representative studies that illustrate the state-of-the-art. First, the author reviews general technology approaches for heavy- and light-duty applications. The presentation reviews: filter technology, covering regeneration strategies, filter properties, durability, and maintenance; nitrogen oxides (NO_X) control by SCR (selective catalytic reduction), LNT (lean NO_X traps), and lean NO_X catalysts; and particulate matter (PM) and NO_X system integration.

In general, progress is impressive and studies demonstrate that high-efficiency systems are within reach in all highway vehicle sectors. Engines are making impressive gains and will increase the options for emission control. Filter technology is focusing on optimization with work being done on better ways to regenerate the filter and improve system back pressure and durability. Mixed mode engine operation provides significant flexibility in this regard, and better control of hydrocarbon species going into the system is a major advancement. SCR NO_X control is focusing on low-temperature performance and system control. LNTs are continuing the rapid evolution of past years with much better sulfur management and new configurations. System integration of filters and NO_X control is currently being road tested for heavy-duty applications using SCR. DPF plus LNTs help prototype light-duty Diesels approach U.S. Tier II Bin 5 standards.

New Diesel Emission Control Strategy for US Tier II and Post Euro IV

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This presentation discusses a new Diesel emission control concept, not only to meet U.S. Tier II and post Euro IV emissions regulations, but also to minimize the fuel consumption (carbon dioxide) penalty.

This system consists of a new combustion control technology and a 4-way catalyst system based on a Diesel particulate filter and lean nitrogen oxides (NO_X) trap. No exhaust port injection system or other special devices are required to realize rich operation with this concept. There is a possibility that today's Diesel engine can transform itself into a 4-way catalyst system with applying only mature gasoline engine technology.

In this work, five representative points of the FTP-75 emissions test cycle were chosen and the emissions and fuel consumption were evaluated using a PSA DW10 2L passenger Diesel engine.

Utilizing Low Temperature Combustion (LTC) and Premixed Controlled Compression Ignition (PCCI) with no post injection, NO_X conversion efficiencies greater than 90 percent were achieved with a minor fuel penalty at every representative point where the break mean effective pressure ranged from 0.8 bar to 8.3 bar. Use of LTC resulted in catalyst bed temperatures above the light-off temperature for the lowest load; and rich, stabilized LTC enabled high NO_X conversion efficiencies at light load. PCCI provided NO_X reductions at high load points. It was confirmed that rich operation, with or without minimal post injection, provided high NO_X conversion efficiencies with only minor fuel penalties.

Urea SCR and DPF System for Diesel LDT/SUV Meeting Tier 2 Bin 5

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Ford Motor Company, with ExxonMobil and FEV, is participating in the Department of Energy's (DOE) Ultra-Clean Transportation Fuels Program with the goal to develop an innovative emission control system for Diesel sport utility vehicles. The focus on Diesel engine emissions is a direct result of the improved volumetric fuel economy (up to 50 percent) and lower carbon dioxide emissions (up to 25 percent) over comparable gasoline engines shown in Europe. Selective Catalytic Reduction (SCR) with aqueous urea as the nitrogen oxides (NO_X) reductant and a catalyzed Diesel Particulate Filter (DPF) were chosen as the primary emission control system components. The program expects to demonstrate more than 90 percent reduction in particulate matter (PM) and NO_X emissions on a light-duty truck/SUV application. Very low sulfur Diesel fuel (~15 ppm) will enable lower PM emissions, reduced fuel economy penalty due to the emission control system, and improved long-term system durability. The end result will allow vehicles with Diesel engines to be Tier II emissions certified at a minimized cost to the consumer.

Third year results showed a 40 percent reduction in engine-out NO_X emissions of a mid-size prototype Diesel engine through engine recalibration and increased exhaust gas recirculation. Use of a rapid warm-up strategy and urea-SCR provided over 90 percent further NO_X reduction, while a catalyzed DPF reduced tailpipe PM levels almost to gasoline vehicle levels. Development work continued to separately improve urea-SCR and DPF system durability. Improvements in exhaust gas NO_X and ammonia sensors were also made for more accurate reductant injection control and on-board diagnostics. Durable hardware was developed, with the help of nozzle and dispenser manufacturers, for delivery of Diesel fuel and aqueous urea simultaneously to the vehicle.

SCR Potential and Issues for HD Applications in the USA

Kuno Flathmann, Detroit Diesel Corp

Stringent emissions standards require complex engine, aftertreatment, and vehicle systems with a high degree of sub-system interaction and flexible control solutions. Among currently foreseeable nitrogen oxides (NO_X) reduction aftertreatment solutions selective catalytic reduction (SCR) is the most mature technology capable of supporting a powertrain to demonstrate near zero NO_X emissions. SCR is being pursued for heavy-duty fleet transportation in Europe and most recently in Japan. This presentation will review the SCR technology and required infrastructure being proposed for customer applications in these markets. The presentation will also review the infrastructure proposed for the U.S. to support this technology for 2007 as well as comment on how the situation changes considering potential implementation for 2010.

A Fast Start-up On-Board Diesel Fuel Reformer for NO_X Trap Regeneration and Desulfation

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The presentation will describe recent progress in our program to develop an emissions technology allowing Diesel engines to meet the upcoming 2007/2010 regulations for nitrogen oxides. At the heart of this technology is the ArvinMeritor Diesel Fuel Reformer that reforms the fuel, on-demand, on-board a vehicle. The fuel reformer uses plasma to partially oxidize a mixture of Diesel fuel and air creating a highly reducing mixture of hydrogen (H_2) and carbon-monoxide (CO). In a previous publication, we have demonstrated that using a reformate rich in H_2 and CO to regenerate a NO_X trap is highly advantageous compared to vaporized Diesel fuel used conventionally. In this presentation we present results and a strategy for performing desulfation of the traps using the fuel reformer. In contrast to vaporized Diesel, which requires very high temperatures that fall outside the normal exhaust operating temperatures for Diesel engines, desulfation was achieved at temperatures around 350°C using the Plasma Fuel Reformer. This is likely to provide substantial durability benefits for the NO_X traps, a major hurdle remaining in the commercialization of that technology. A lower temperature that falls within the normal engine operating range also provides an effective desulfation strategy including the possibility of some desulfation occurring simultaneously with NO_X regeneration. In this presentation, experimental results will also be presented on the fuel reformer including hydrogen yield, soot production, start-up time, and durability. The fuel reformer is capable of reaching up to 90 percent of the theoretically possible hydrogen yield at a range of fuel flow rates when used in conjunction with a downstream catalyst. The soot production is minimal both upstream (<20 mg/m^3) and downstream (< 5 mg/m^3) of the catalyst, while the start-up time required to reach 90 percent of the maximum hydrogen output is around 5 seconds. The system has been operated for more than 5000 cycles without any noticeable performance degradation.

Impact of SO_2 on Lean NO_X Trap Catalysts

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The use of Lean NO_X Trap (LNT) catalysts to reduce greenhouse gas and nitrogen oxides (NO_X) emissions from lean-burn gasoline and Diesel engines is an appealing idea due to the low impact of infrastructure deployment compared to competing technologies. However, performance issues and (particularly) durability of catalysts are key barriers to the commercial acceptance of LNT catalysis for Diesel aftertreatment. Pt-BaO/γ-Al_2O_3 is a promising LNT formulation. However, deactivation of this benchmark material by sulfur oxides is severe, hence the need to improve durability. We have chosen to study the effect of copper on Pt-BaO/γ-Al_2O_3 based on its demonstrated ability to impart sulfur tolerance to related catalyst systems. The resistance of Pt-BaO/γ-Al_2O_3 (1 wt.% Pt, 20 wt.% BaO) and Pt-Cu-BaO/γ-Al_2O_3 (1 wt.% Pt, 2 wt.% Cu, 20 wt.% BaO) to deactivation by sulfur dioxide (SO_2) addition was investigated during both lean and rich cycles at 380°C. Our results showed that addition of copper to the benchmark catalyst decreased the initial storage capacity of NO_X on the catalyst; however, it also slowed its deactivation by SO_2. Additional characterization of the materials suggests that the improved sulfur tolerance results from the formation of bimetallic Cu-Pt phases.

Use of a Diesel Fuel Processor for Rapid and Efficient Regeneration of Single Leg NO_X Adsorber Systems

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Nitrogen oxides (NO_X) adsorber or NO_X trap systems must be regenerated frequently to convert the adsorbed NO_X to nitrogen and to regenerate the NO_X adsorption capacity of the NO_X trap. This regeneration requires a reducing environment and the presence of a reductant capable of reacting with the NO_X trap components. Numerous reports have shown that "reactive" reductants such as hydrogen, carbon monoxide, and oxygenated species can regenerate NO_X traps more rapidly and at lower temperatures than with direct Diesel injection. While this offers a clear NO_X reduction advantage, providing such a reductant in a cost effective manner can be problematic.

A cost effective Diesel fuel processor has been developed that can operate from low loads to full load. The fuel processor can produce periodic high concentrations of a "reactive" reductant as required during the regeneration cycle. Full-scale engine tests with several different origioinal equipment manufacturers have shown that the fuel processor produces a "reactive" reductant over a wide exhaust temperature range and with good control of reductant mass flux. The benefits of a reactive reductant were demonstrated by tests in which the NO_X trap was regenerated with reductant pulses as short as 1 second. Steady state tests have shown fuel penalties of less than 3 percent for a single leg system with greater than 90 percent NO_X conversion. The operating characteristics and performance of the Diesel fuel processor will be presented.

High Throughput Program for the Discovery of NO_X Reduction Catalysts

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Gerald Koermer
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This project for the discovery of new lean nitrogen oxides (NO_X) catalysts is now into its second year and, using high throughput techniques, is searching through many materials very rapidly to find new catalyst prospects. The Engelhard discovery system has been modified and has been active since May of 2003. Material scale up techniques to evaluate promising candidates in the GM reactor have been developed and implemented. The GM reactor has been modified and has been used in validation studies. Validation shows that the discovery reactors and the GM reactor are good techniques for describing the response of a catalyst to Diesel engine conditions. A secure network for database population is operational and the database is being populated. Over 2,000 materials have been evaluated and approximately 10 percent of those materials have been identified for detailed analysis in the GM reactor. Informatics software for data import, a database, search and query tools and trend analysis has been developed. Trend analysis and design of experiment are being used to refine the search for high activity NO_X reduction catalysts. This presentation will be a report on the progress of the program.

Economic Comparison of LNT versus Urea SCR for Light Duty Diesel Vehicles in US Market

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Lean NO_X trap (LNT) and urea selective catalyst reduction (urea-SCR) catalysts are under development for nitrogen oxides (NO_X) reduction. In this paper, we compare the total cost effects of choosing LNT versus urea-SCR for NO_X reduction. The input data used for this analysis is developed from publicly available sources.

To estimate the costs, we first describe typical systems in terms of catalyst size and loading, and added required equipment such as additive dosing systems and control sensors. From these descriptions we develop cost estimates. The high precious metal loading and volume typical of LNT catalysts makes those systems significantly more expensive than urea-SCR, even after including a urea dosing system.

Further, LNT strategies involve periodic rich regeneration, causing degradation in fuel efficiency. Since manufacturers must meet Corporate Average Fuel Economy (CAFÉ) standards, any degradation in vehicle fuel efficiency for some vehicles must be offset by improvements in the fuel efficiency of other vehicles. Using estimates of Diesel vehicle market penetration along with the cost to improve fuel efficiency, we can estimate the expenditure required to offset the LNT fuel economy penalty.

The cost of vehicle ownership is affected by fuel consumption and, in the case of urea-SCR, urea purchase costs. The cost of added fuel consumption for LNT more than offsets a likely urea cost.

Of course, urea-SCR system function requires the vehicle to have urea available onboard. Estimates of the cost of a urea co-fuelling infrastructure are made.

The total cost to provide urea co-fuelling infrastructure is roughly equivalent to about three years' cost increase for LNT over urea-SCR. That is, total cost to society is lower after three years when urea-SCR systems are used, even choosing the most expensive urea infrastructure option.

Use of urea-SCR offers better fuel efficiency and lower greenhouse gas emissions, higher and more robust NO_X conversion, much lower aftertreatment system cost, and lower cost of ownership. Business, consumers, and government should work together to enable urea-SCR technology.

Development of a Durable Low-Temperature Urea-SCR Catalyst for CIDI Engines

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In the quest for effective emission control devices for compression ignition direct injection (Diesel) engines, Selective Catalytic Reduction (SCR) using urea lies ahead of most other technologies due to its high nitrogen oxides (NO_X) reduction efficiency. It is well documented, however, that the performance of SCR catalysts drops precipitously at low temperatures (typically <250°C), leaving emissions control for light-duty (LD) Diesels unsolved. We have embarked upon the development of an active and durable low temperature urea-SCR catalyst that could enable regulatory acceptance of LD Diesel vehicles (*e.g.*, SUVs, light-duty trucks). Active component development has deliberately steered away from the use of vanadium, a highly active yet toxic metal. Our catalyst formulations are based on transition metals supported on hydrous metal oxide substrates. Activities screening utilized granulated powder catalysts, while promising formulations were transferred to monolith platforms in house for further evaluation. Comparison of powder and monolith data verified that, under the experimental protocols employed, monolith performance could be accurately predicted from data collected using powders. Some successful candidates that meet all of the performance requirements of original equipment manufacturer collaborators have been developed and subjected to a number of durability tests. Fresh, degreened performance was evaluated using simulated LD-Diesel exhaust, with ammonia as the reductant, across a range of temperatures (125 – 450°C), $NO:NO_2$ ratios, and space velocities. Durability tests were conducted on the best-performing candidates, and included evaluating catalytic activity after high-temperature hydrothermal treatment, exposure to hydrocarbons, and exposure to sulfur dioxide. The results show that the addition of a promoter to specific formulations results in catalysts that meet all activity and durability targets.

Review of SCR technology for Diesel Emission Control: European experience and perspectives for 2010

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Aaqius & Aaqius

Selective catalytic reduction (SCR) technology has been used to control emissions from stationary sources for more than 20 years. More recently, it has been applied to selected mobile sources, including heavy duty-trucks, marine vessels, and locomotives. In October 2005, SCR is expected to be introduced in Europe targeting on-road Diesel heavy-duty vehicles (HDV) to help meet the Euro 4 emission standards.

This presentation describes the current roadmap of SCR in Europe in the HDV segment and reviews all key elements of this technology. A European market overview will be presented describing the implementation of the SCR in terms of infrastructure, cost, efficiency, architecture, and vehicle integration for HDV. Some forecasts will be developed for light-duty vehicles in order to comply with future standard regulations, Euro V/VI and US10.

Decomposition and Storage Phenomena of Urea in SCR Systems

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Continued interest in the benefits of high efficiency lean burn engines for light-duty and some heavy-duty applications has challenged exhaust aftertreatment with operation at low temperature. Concerns over durability of nitrogen oxides (NO_X) adsorber catalysts have re-invigorated interest in urea-SCR (selective catalytic reduction) for light-duty Diesel applications. In several studies of SCR systems on light-duty and heavy-duty Diesels, urea decomposition and SCR performance has been investigated. Experiments were carried out using a 1.7L four-cylinder common rail injected Diesel engine as well as a 5.9L medium-duty Diesel to generate exhaust for the SCR devices. Urea injections at stoichiometric levels and below were used. Measurements of NO_X performance, urea hydrolysis, and unregulated emissions such as dinitrogen oxide, nitrates, nitrites, and ammonia, were made. Additionally, instrumentation and sample collection challenges are described. Long duration exposures and burn-off studies revealed the long time scale storage of ammonia and ammonia precursors at low temperatures. Results indicated that there was very significant storage of ammonia in the form of ammonium nitrate and isocyanic acid at temperatures below 180°C. These storage and release phenomena have important implications for model-based control of the urea-SCR process. Higher temperature operation and over-spray led to formation of several identifiable urea decomposition products.

Diesel Aftertreatment Systems Development

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The use of aftertreatment will be required to meet future heavy-duty exhaust emission regulations. A systems-level development approach will be necessary to fully evaluate both the potential benefits of aftertreatment as well as the technical challenges that require additional focus. Catalyst bench test facilities, engine testing capability, and a combination of device- and system-level modeling tools have been developed. These capabilities have been applied to evaluate the integration of advanced aftertreatment devices with Advanced Combustion Emission Reduction (ACERT) technology.