

II.B.5 Crosscut Lean Exhaust Emission Reduction Simulation (CLEERS)

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The following report is for three separate activities that are included under CLEERS:

- Administrative support (Stuart Daw and Sreekanth Pannala)
- Joint development of benchmark kinetics (Stuart Daw, Kalyana Chakravarthy, Katey Lenox, Jae-Soon Choi, and Jim Parks)
- Micro-scale catalyst modeling for performance and durability (Bill Shelton and Sreekanth Pannala)

Objectives

Administrative Support

Provide coordination of the CLEERS activity for the Diesel Crosscut Team in accomplishing the following:

- Promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems.
- Promote development of performance models for emissions control components such as exhaust manifolds, catalytic reactors, and sensors.
- Provide consistent framework for sharing information about emissions control technologies.
- Help identify R&D needs and priorities.

Joint Development of Benchmark Kinetics

- Coordinate ORNL's collaboration with Pacific Northwest National Laboratory (PNNL) and Sandia National Laboratories (SNL) in the development of kinetics information needed for aftertreatment component simulation.
- Provide benchmark laboratory measurements of NO_x reduction chemistry and reaction rates.
- Coordinate laboratory measurements of lean NO_x trap (LNT) materials with ongoing test-stand/vehicle studies in the NTRC facility.
- Develop and validate global chemistry and (low-order) models for LNT kinetics.

Micro-Scale Catalyst Modeling

- Develop a simplified computational model that relates the effects of catalyst surface morphology on the chemistry and performance of critical aftertreatment components.
- Utilize this model in combination with experimental performance data and microscopic surface characterizations to correlate and predict trends in aging, sulfur poisoning, and component regeneration.

Approach

Administrative Support

- Set up and coordinate meetings of the CLEERS Planning Subcommittee;
- Co-lead the LNT Focus Group.

- Provide overall coordination and secretarial assistance in planning and carrying out the CLEERS public workshops.
- Maintain the CLEERS website on an ORNL server accessible via the internet.
- Provide periodic status updates and summary reports to the Crosscut Team.
- Respond to general requests and inquiries about CLEERS from the public and technical community.

Joint Development of Benchmark Kinetics

- Maintain regular interactions with PNNL and SNL through the Focus Groups and direct meetings.
- Conduct experimental measurements of LNT chemistry and reaction rates using the pre-competitive adsorber materials in the ORNL bench-flow and diffuse reflectance infrared spectroscopy (DRIFTS) reactors.
- Analyze test-stand/vehicle LNT data collected at the NTRC facility, and compare this data with the laboratory bench-flow and DRIFTS measurements.
- Write and validate simplified computer LNT codes that can be used to evaluate the laboratory and test-stand rate measurements.
- Publish and post experimental/modeling results from ORNL in journals and on the website.

Micro-scale Catalyst Modeling

- Develop a computer code that uses a simplified rule-based Monte Carlo process to simulate surface morphology changes in supported catalysts as they age and the impact of those changes on reaction conversion efficiency.
- Initially apply the code to simulating LNT aging and sulfur poisoning.
- Validate the code predictions with experimental data.
- Apply the results of the Monte Carlo simulations to global LNT performance models.

Accomplishments

Administrative Support

- Co-led the CLEERS Planning Committee.
- Assisted in completing organization and implementation of the Selective Catalytic Reformer (SCR) Focus group.
- Co-led LNT Focus Group, and provided assistance as needed for diesel particulate filter (DPF) and SCR Groups in their regular meetings.
- Provided regular update reports to the DOE Diesel Crosscut Team.
- Held 7th CLEERS workshop at Detroit Diesel Corporation on June 16 and 17.
- Collaborated with supplier representatives and LNT Focus Group to develop a draft bench characterization protocol for LNT materials that is intended to provide the basis of standard kinetic ‘maps’ (i.e., data templates) for communicating critical simulation properties. Presented the protocol at the 7th CLEERS workshop and posted on the website.
- Expanded website functionalities, security, and data to facilitate web meetings and serve Focus Group interactions.

Joint Development of Benchmark Kinetics

- Developed LNT kinetic map characterization protocol in conjunction with the LNT Focus Group and collaborating suppliers.
- Acquired first available commercial LNT material from Umicore as a standard benchmark material and initiated degreening and detailed chemical analysis.
- Acquired Toyota DPNR (Diesel Particulate NO_x Reduction, combined LNT and DPF aftertreatment) and LNT samples from Ford and initiated chemical analysis and bench testing.

- Completed simplified global models of LNT capture and regeneration. Described models in public presentations and publications. Posted MATLAB code that implements these models on the website.
- Extensively upgraded the ORNL bench-flow reactor to ensure compliance with key requirements of the draft characterization protocol.

Micro-Scale Catalyst Modeling

- Developed rules-based Monte Carlo code that better simulates sintered Pt particle distributions within Pt islands as well as the distribution of the Pt islands.
- Implemented and tested a new rules-based NO_x chemistry module interfaced with the Pt sintering code.

Future Directions

Administrative Support

- Continue co-leading CLEERS planning committee.
- Continue co-leading the LNT Focus Group and support the DPF and SCR Focus Groups as needed.
- Continue providing standard reference LNT materials and data for Focus Group evaluation.
- Organize 8th CLEERS workshop sometime after March 2005.
- Continue maintenance and expansion of CLEERS website.
- Continue providing regular update reports to the DOE Diesel Crosscut team.

Joint Development of Benchmark Kinetics

- Complete improvements to the ORNL bench-flow reactor.
- Demonstrate draft LNT characterization protocol on ORNL bench-flow reactor and identify needed revisions and technical issues.
- Complete bench reactor measurements, DRIFTS reactor measurements, chemical analysis, and microscopic characterization of Umicore LNT reference material. Transmit these results to the LNT Focus Group as they become available.
- Update and post revised global LNT model with input from SNL, literature, and ORNL experimental data as these become available.
- Complete chemical analysis, powder and bench-flow reactor measurements, and microscopic characterization of the Toyota DPNR and LNT samples.
- Coordinate kinetic and microscopic characterization measurements with LNT durability tests developed under the rapid aging protocol.

Micro-Scale Catalyst Modeling

- Derive mean-field approximations that can be used to speed up simulations.
- Refine the Pt particle coarsening rules to correlate with microscopy measurements of the LNT model and reference materials.
- Include explicit steps for sulfur poisoning in aging simulation.
- Use combined Monte Carlo code to produce relative rate parameters that can be used in global performance models for studying the impact of different operating and control strategies.

Introduction

Improved catalytic emissions controls will be essential for utilizing high-efficiency lean-burn engines without jeopardizing the attainment of the U.S. Environmental Protection Agency heavy-duty

engine emission standards scheduled to take effect in 2007. Simulation and modeling are recognized by the DOE Diesel Crosscut Team as essential capabilities needed to achieve this goal. In response to this need, the CLEERS activity (Crosscut Lean Exhaust Emissions Reduction Simulation) was

initiated to promote development of improved computational tools for simulating realistic full-system performance of lean-burn engines and the associated emissions control systems. While CLEERS does not directly support the development of extensive full-emissions-system performance simulation codes, it does provide explicit support for the following activities:

- Public workshops on key emissions control topics;
- Collaborative interactions among and between Crosscut Team members, emissions control suppliers, universities, and national laboratories under specially organized topical focus groups;
- Development of experimental data, analytical procedures, and computational tools that are directly useful for understanding component performance and the behavior and durability of catalytic materials;
- Development of consistent frameworks for sharing information about emissions control technologies; and
- Development of explicit recommendations to DOE and the Diesel Crosscut Team regarding the most critical emissions control R&D needs and priorities.

ORNL is involved in three separate DOE-funded tasks that support CLEERS:

- Overall administrative support;
- Joint development of benchmark LNT kinetics with SNL and PNNL; and
- Micro-scale catalyst modeling for performance and durability.

In the administrative task, ORNL staff members coordinate the CLEERS Planning Committee, the CLEERS Focus groups, the public workshops, and the CLEERS website (www.cleers.org). The joint kinetics development task involves collaboration among ORNL, SNL, and PNNL to produce key kinetics information needed for predicting the performance of lean NO_x adsorbers and catalyzed particulate filters. The results of this work are discussed with the LNT and DPF Focus groups prior to publication to provide technical review and guidance to the labs. The collaboration is structured to build on the strengths of each lab and leverages

against other DOE-funded activities to maximize benefits. The micro-scale modeling task is intended to help improve understanding of catalyst morphology, how changes in that morphology relate to aging, and how those changes affect practical component performance.

Approach

Administrative Support

In FY 2004 ORNL has continued acting as the lead coordinator of the overall functions of the CLEERS Planning Committee and Focus Groups. Stuart Daw of ORNL is responsible for providing general assistance to each of the Focus Groups and is a co-leader (with Dick Blint of General Motors) of the LNT Focus Group. George Muntean and Darrell Herling from PNNL are co-leaders of the DPF and SCR Focus Groups, respectively, and report on their activities elsewhere. ORNL organizes and implements the public workshops under guidance from the Focus Groups and Planning Committee, providing both technical and secretarial support. The CLEERS website is maintained (under direction of Sreekanth Pannala) on an ORNL server accessible via the internet. Both public and restricted areas have been set up on this website to facilitate distribution of technical information, workshop information and presentations, and interactive web meetings. Stuart Daw provides assistance to Dick Blint (GM) in presenting periodic status updates and summary reports to the Crosscut Team. Both Stuart and Sreekanth Pannala at ORNL respond to general requests and inquiries about CLEERS from the public and the technical community.

Joint Development of Benchmark Kinetics

ORNL's responsibility in this activity is to set up and conduct experimental measurements of LNT chemistry and reaction rates that will help to define the critical physical characteristics of LNT materials responsible for determining practical performance (i.e., NO_x emissions reduction and energy efficiency). In this function, ORNL utilizes reference non-competitive adsorber materials in the ORNL bench-flow and DRIFTS reactors. Where possible, these bench measurements are also supplemented with other specialized measurement

capabilities such as high-resolution microscopy at the ORNL High Temperature Materials Laboratory (HTML). ORNL maintains regular interactions with PNNL and SNL and the industry collaborators through the LNT Focus Group in order to maximize the value of the data generated and provide feedback that can be considered in planning future experiments. Where possible, laboratory results are compared with and analyzed in the context of test-stand/vehicle LNT measurements generated in parallel projects at ORNL's NTRC facility. For assistance in interpreting trends, ORNL has been writing and validating simplified computer LNT codes that can be used to evaluate the laboratory and test-stand data. Results are published in peer-reviewed journals, presented in public meetings, and/or posted on the CLEERS website.

Micro-Scale Catalyst Modeling

In this activity, ORNL is applying previously developed methods for rule-based Monte Carlo simulations to construct a computer code that can capture the key physics of surface morphology changes that occur in supported catalysts (initially specifically for LNTs) as they age. In addition to reflecting the changes in morphology, the code is designed to reflect the impact of these changes on NO_x conversion efficiency and reductant consumption in terms of global rate parameters that can be used in system simulations. The target phenomena at this stage are Pt particle sintering (coalescence) and sulfur poisoning. Validation of the predicted trends with experimental data is an important aspect of the approach (as data become available). In regard to the latter, we have begun to closely coordinate with the rapid aging protocol development started in FY 2004.

Results

Administrative Support

The seventh CLEERS workshop was held June 16 and 17 at the Detroit Diesel Corporation training facility in Detroit. All three emissions control technology areas (LNTs, DPFs, and SCR) were covered, but the greatest emphasis was on DPFs and SCR. The complete technical program, meeting summary, and most of the presentations are available

on the website (www.cleers.org). More detailed summaries were also provided to the Diesel Crosscut Team. This was the largest workshop to date, with a total of 90 registrants. This attendance also included very large participation from emissions control suppliers as well as original equipment manufacturers (OEMs).

The LNT and DPF Focus Groups have been holding regular phone/web meetings throughout the year, and summary reports of the meetings have been provided to the Diesel Crosscut Team. Darrell Herling from PNNL and Joe Bonadies from Delphi agreed to serve as co-leaders for the SCR Focus Group, and this group began meeting in May.

One of the main activities of the LNT Group has been the development of standard kinetic "maps" or "templates" that can be transferred between suppliers and users. Direct involvement of the suppliers was initiated with assistance from Joe Kubsch at Manufacturers of Emission Controls Association (MECA). Supplier representatives from Delphi, Johnson Matthey, Engelhard, 3M, Tenneco, and Arvin Meritor have participated in meetings with a subcommittee from the LNT Group composed of Dick Blint (GM), Neal Currier (Cummins), Ed Jobson (Mack/Volvo), and Stuart Daw (ORNL). As a result, considerable progress was made in defining a set of 74 bench flow reactor conditions to be used as the basis for the kinetic maps. This list of specified conditions was publicly distributed at the seventh CLEERS workshop and on the website in June. It is expected that the standard conditions can be used to define a minimal characterization of the key features of each LNT sorbent material being considered by OEMs. With this information, OEMs should be able to obtain reasonably accurate performance predictions using their in-house LNT models. Field demonstrations of the feasibility and applicability of the LNT bench reactor characterizations at multiple LNT Focus member sites are now underway.

The LNT Group has agreed to concentrate initial testing of the protocol on LNT samples provided by Umicore of their European commercial product intended for gasoline direct injection (GDI) applications. Because these samples are commercial, complete physical and chemical characterizations

can be made to correlate with the bench measurements. ORNL will also make comparisons between this material and other LNT materials being tested at ORNL in other activities, including standard Ba-type model materials made at ORNL and prototype MECA materials (for which detailed physical and chemical characterizations are unavailable). Ford has also supplied a sample of DPNR material from the Toyota Avensis vehicle to ORNL for evaluation. Results from this material will be shared with the LNT Group as they become available.

The DPF Group has been using the experience of the LNT Group as a guide for developing their own concept of DPF performance ‘maps’. They have decided to consider both defining a test matrix of characterization procedures for the DPF materials as well as developing actual performance trends from model simulations to help guide the analysis and understanding of DPF function. George Muntean provided a presentation summarizing these approaches at the March Diesel Crosscut Meeting. One of the major technical difficulties with DPFs will be to decouple filter loading and regeneration since loading affects soot distribution and cake properties, which then influence regeneration. The question has been raised whether engine tests can be minimized for DPFs as they were in the LNT test matrix. Engine tests may be necessary to obtain realistic soot loading. Engine operating conditions, such as steady state vs. dynamic, can affect soot quality (ash content, organic carbon/elemental carbon ratio) via changing oil consumption. It was suggested that a filter might be loaded on an engine and then regenerated in a reactor. Other practical issues under consideration are the observations that soot seems to age and that filter regeneration properties may vary over time (i.e., vary with time after loading). The DPF Group has formed a subcommittee charged with defining the objectives and general approach needed to characterize particulate filters. One emerging conclusion thus far is that DPF characterizations are likely to require a significant amount of testing on actual engines as opposed to laboratory bench reactors. This will be a significant departure from the LNT and SCR protocols, which are mainly focused on bench reactor measurements.

In the SCR Group, Ford has proposed their list of characterization protocol measurements for urea-SCR materials as a starting point. Measurements such as those proposed by Ford would appear to be relatively simple because they are made at steady-state conditions without the need to resolve detailed dynamic transients. The Group has also found a supplier that appears willing to supply a commercial zeolite-type SCR catalyst that can be used as a shared reference by the group (similar to the Umicore material used by the LNT Group). The SCR Group has also spent considerable time defining the performance features that need to be captured by the characterization protocol and simulations.

Joint Development of Benchmark Kinetics

Early in 2004, the ORNL bench flow reactor was modified to include a higher-speed switching system that allowed more rapid transitions between lean and rich conditions. Experience has shown that the observed breakthrough profiles can be strongly affected by the lean/rich transition time, with the optimal time being as fast as possible. Even with these changes, the transition between lean and rich states took as long as two seconds to be completed. The spatially resolved capillary inlet mass spectrometry (SpaciMS) instrument has turned out to be very useful for determining this response time. Example results illustrating this fast response for hydrogen breakthrough are shown in Figure 1.

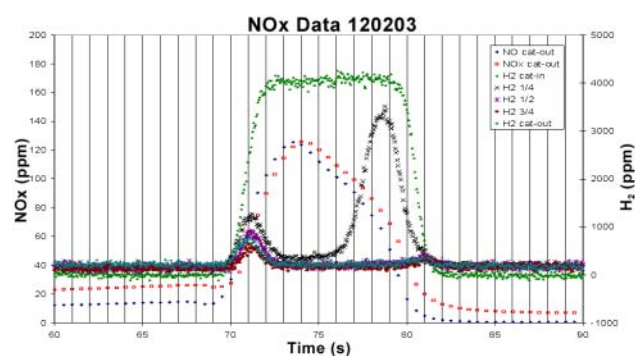


Figure 1. Hydrogen breakthrough profiles for a SCONO_x-type (SCONO_x is the brand name of a lean NO_x trap catalyst containing potassium made by Emerachem) catalyst in the bench flow reactor as measured by SpaciMS. NO_x breakthrough profiles measured by conventional gas analyzers are shown for comparison.

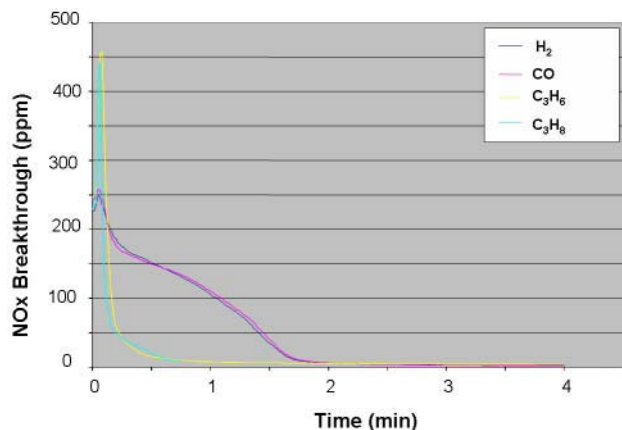


Figure 2. NO_x breakthrough for regeneration of the first model sorbent with different reductant species. The capture and regeneration times were set very long in these experiments to accentuate differences.

Two different model sorbents containing barium as the primary alkali sorbent species were produced in monolith form, both as full bricks and as core samples for the bench reactor. Bench testing of these materials is still underway, and engine testing of the full bricks is planned for next year. Preliminary bench flow results for different reductant species (hydrogen, CO, propane, and propylene) have shown large differences in response for the first model sorbent. Example breakthrough profiles illustrating these results are shown in Figure 2. These differences illustrate the importance of having reliable methods for characterizing and defining the different species effects in accurate simulation models.

Direct comparisons are now being made between the bench flow characteristics of the candidate sorbents and the engine/dyno performance seen in the DaimlerChrysler 1.7-liter LNT tests. Using the high-speed switching system to transition between lean and rich conditions on the bench reactor, we are now able to nearly reproduce the cycling conditions of the engine tests. In addition to the model barium-containing sorbents described previously, we have also begun experiments with sorbents supplied by MECA. Such comparisons between the laboratory and bench scale measurements have been extremely helpful in improving our understanding and models of capture and regeneration.

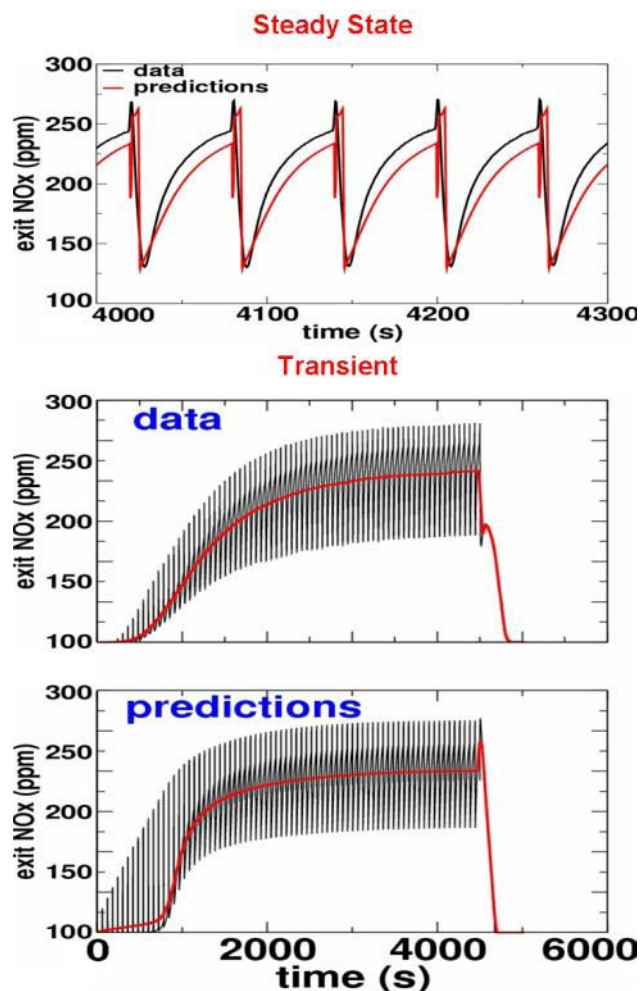


Figure 3. Observed and predicted NO_x breakthrough profiles for a MECA catalyst in the bench flow reactor during fast lean/rich cycling (55 s lean/5 s rich). The reductant in this case is 0.2% hydrogen, and the inlet NO concentration is 300 ppm during the lean period. The sorbent is clean (no stored NO_x) at the beginning of the experiment. The transient plots compare the predicted and observed long-term NO_x breakthrough trends as the sorbent loads up, while the steady-state plot compares the details of NO_x breakthrough for individual cycles.

By estimating the thermodynamic properties and global kinetics from the bench reactor measurements and then implementing them in an integral reactor model, we are able to quite closely reproduce the observed sorbent performance for all the materials evaluated. For example, Figure 3 illustrates the NO_x breakthrough observed in the bench reactor under fast cycling conditions and compares the observation

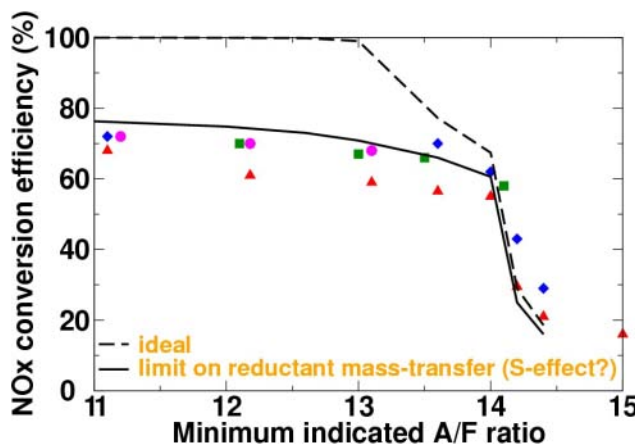


Figure 4. Observed and predicted engine/dyno LNT NO_x conversion (overall) as a function of the level of richness during regeneration. The MECA sorbent in this case was heavily sulfated. Richness is indicated in terms of the engine-out universal exhaust gas oxygen sensor indicated air/fuel ratio. Note the limit in performance at increasing richness. This can be replicated by the model only by adding a finite limiting rate for reductant diffusion during regeneration.

with corresponding predictions from our global kinetics model.

The global kinetics and integral reactor models have also provided guidance in interpreting the observations from the engine/dyno experiments. Essentially, these models are based on the differential mass balances for NO_x, O₂, and reductant species, which are then integrated along the reactor over time. For example, in Figure 4, the conversion performance of a highly sulfated LNT is shown as a function of the richness of the regeneration pulse produced by in-cylinder fuel modulation (as indicated by the engine-out universal exhaust gas oxygen sensor). Note that as the richness is increased (lower as-indicated air/fuel ratio), a definite limit in overall NO_x conversion of 60-70% is reached. Further increases in richness with this regeneration strategy did not improve conversion and succeeded only in wasting fuel. By applying our integral global kinetics model, we have been able to determine that the performance limit is the result of a zeroth-order rate limit on the reduction reaction. This limit appears to be significantly reduced by the high degree of sulfur poisoning. Now that this limit has been recognized, the specific physical causes and

correlation with sulfur poisoning can be more effectively investigated.

Additional details of the global kinetics model have been summarized in publications and posted on the CLEERS website. We are also using the insights provided by the model and bench and engine/dyno experiments to help improve the effectiveness of the standard characterization matrix for LNT characterization being developed by the CLEERS LNT Focus Group. The latter is intended as a minimal set of reference data that can be provided by suppliers to OEMs for each sorbent material. It is expected that OEMs will be able to use this data with their in-house models to estimate performance trends for candidate materials and evaluate options for emissions control system designs and control strategies.

Meetings were held in March between ORNL and SNL staff to further define the details of our collaboration for modeling the multiple reaction steps involved in determining the observed global rates for capture and regeneration. One particular area of interest is in the loss of reactive surface area on the Pt-group metals in the sorbent. Bench reactor data at ORNL suggests that there may be a gradual surface oxide formation (i.e., oxygen poisoning) that limits NO_x storage during the lean period. Likewise, it may be possible that NO_x reduction may become limited by a similar surface sulfide formed during regeneration. Tony McDaniel is investigating how previous kinetics studies of oxide and sulfide formation on Pt may be applied to the LNT context.

Additional hardware modifications were made later in the year to the ORNL bench flow apparatus in order to accommodate the expected requirements of the standard LNT protocol. Specifically, a faster valve was added for the lean/rich cycling mechanism, and inlet and outlet couplings for the quartz reactor tube were redesigned to reduce the potential for leaks. Considerable effort is also being spent on calibrating the dynamic responses of the NO, NO_x, CO, O₂, and Fourier transform infrared (FTIR) analyzers in order to be able to make the needed measured breakthrough corrections. Recent studies have included extensive use of SpaciMS measurements of NO_x, O₂, and H₂ breakthrough profiles at 5 axial locations.

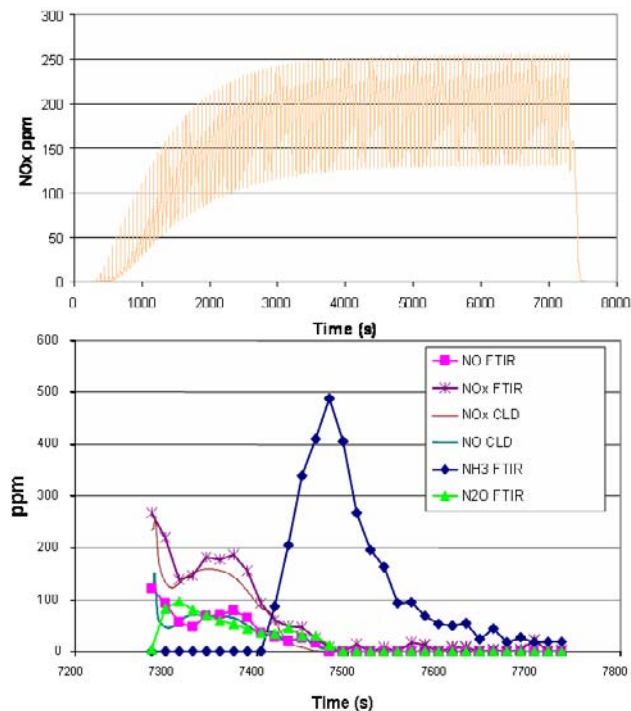


Figure 5. Observed breakthrough profiles for a MECA candidate sorbent during fast cycling followed by a deep regeneration. The fast cycling conditions were 55 s lean (with 300 ppm NO in simulated exhaust) and 5 s rich (with 0.5% H₂). At the end of fast cycling, the 0.5% H₂ condition was continued without interruption. The lower plot is an enlargement of the measurements for the latter period.

A simplified MatLab version of the global NO_x breakthrough model that has been used to successfully match the observed bench reactor performance so far is now posted on the CLEERS website for public downloading. While it has many shortcomings, we believe this model can serve as a basis for sharing information and developing improved methods for reconciling protocol data from different bench flow reactors (e.g., reactors with different space velocities and length/diameter ratios). It also may be possible in the future to utilize this or a similar model to serve as a basis for ‘compressing’ the standard protocol measurements (i.e., fitting the measured breakthrough profiles to the global model with a relatively small number of global rate parameters that can then be used in place of the original data). Perhaps more generally, it may be

possible to use these parameters to compare the responses of different materials.

Although the global LNT model appears to be useful for correlating overall NO and NO₂ breakthrough, recent observations indicate that N₂O and NH₃ can also be produced in significant quantities during NO_x regeneration. This can be observed in Figure 5 for a fast cycling case with the MECA prototype sorbent where a ‘deep’ reduction condition is imposed at the end of a large number of repeated lean/rich cycles. Under these conditions, we observe both a large pulse of N₂O and a large pulse of NH₃, indicating that there is some type of long-timescale, complex storage of nitrogen compounds on the sorbent surface leading to a significant and unexpected loss in NO_x conversion to N₂. This general behavior has been observed for both H₂ and CO reductants, indicating that it is not specific to regeneration strategies that favor either species. Recent discussions in the LNT Focus Group have confirmed that others have seen similar releases of N₂O and NH₃ even during fast cycling. Clearly, these byproduct species will be of great importance in realistic applications and need to be included in subsequent versions of the LNT model.

During the summer, post-doc Jae-Soon Choi was able to complete extensive use of SpaciMS measurements of NO_x, O₂, and H₂ breakthrough profiles at 5 axial locations. Figure 6 illustrates the kind of information made available by the SpaciMS measurements; specifically, it is possible to observe the transitions in the shape of the concentration profiles as the species fronts move axially down the channel. This type of information is extremely useful in improving and validating LNT models that address the effects of reactor length on performance.

Micro-Scale Catalyst Modeling

The development of a continuously distributed NO_x storage site model that includes the effects of precious metal coarsening is necessary to understand the aging process and interpret microscopy experiments. This year we developed a model that better captures the realistic particle distribution within a Pt island as well as distribution of the islands. This new approach better represents the experimentally observed behavior. This process also

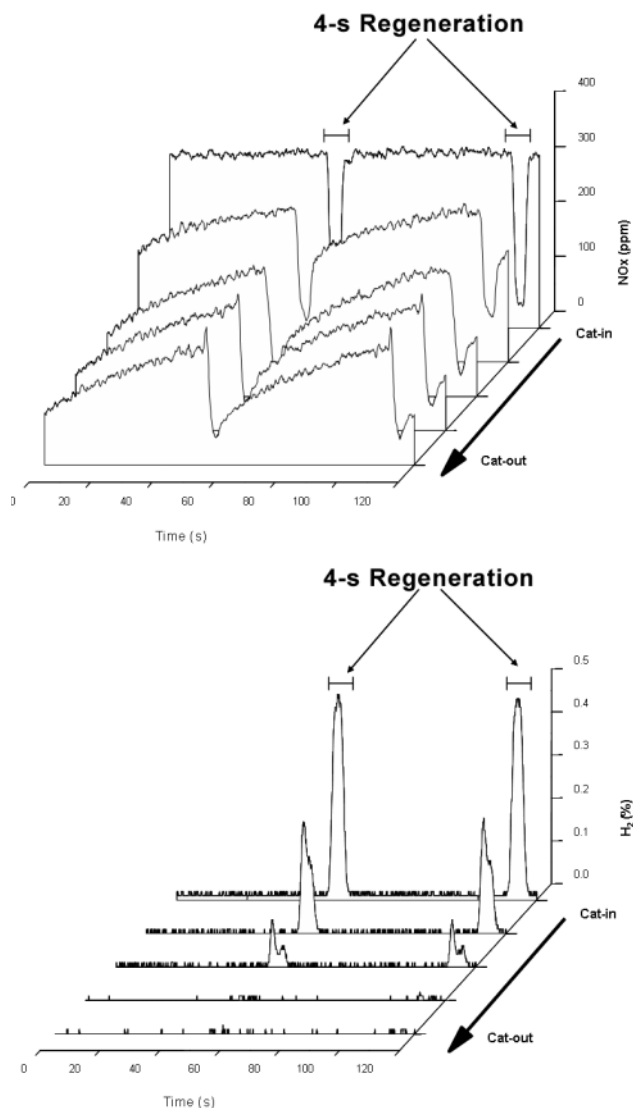


Figure 6. Plots illustrate the transient breakthrough of NO_x and hydrogen at different axial locations in a potassium sorbent LNT monolith as measured with SpaciMS. The LNT sample is mounted in the ORNL bench reactor and is being cycled for 56 s under lean conditions (12% O₂, 5% H₂O, 300 ppm NO) and 4 s under rich conditions (0% O₂, 5% H₂O, 0 ppm NO, 0.5% H₂) at a space velocity of 25000 h⁻¹ and 200°C.

includes two competing coarsening and de-coarsening steps. Currently, the rule used in the de-coarsening step is based on a probability distribution that scales inversely with particle size, and additional distributions are being explored.

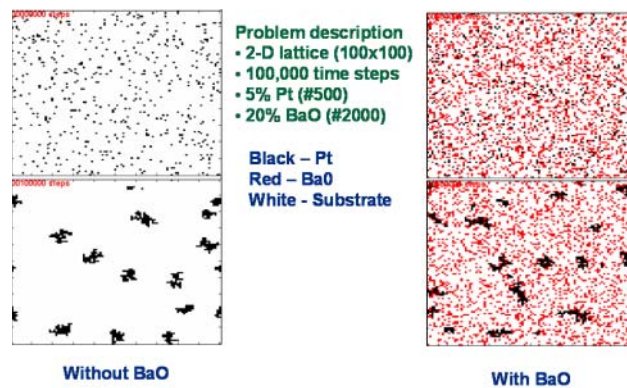


Figure 7. Platinum Coarsening With and Without BaO

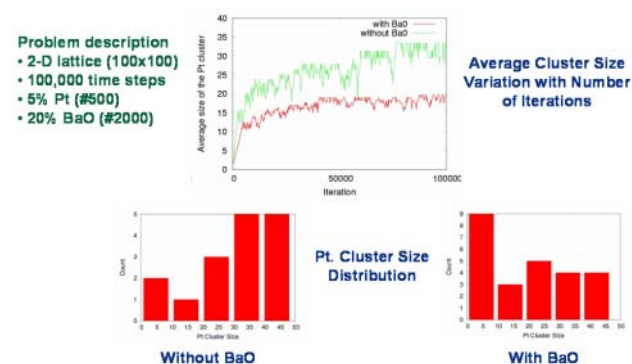


Figure 8. Platinum Cluster Size Distribution and Evolution of Average Size of the Pt Cluster With and Without BaO

In addition, post-processing tools have been added to visualize the coarsening effects and also to track the particle size distribution with time. To validate the code, we are performing both small-scale (10,000 cells) and large-scale (500,000 cells) systems simulations for long timescales and comparing to available experimental data. This work has been presented at the 7th CLEERS workshop held in Detroit, and sample results are shown in Figures 7 and 8. In Figure 7, Pt coarsening with and without BaO are plotted (the upper plots are the initially dispersed condition, the lower plots are after 100,000 Monte Carlo iterations). The simulations reproduce the experimentally observed behavior that Pt coarsening is inhibited by the presence of BaO. In Figure 8, both average cluster size variation with time and probability density function of Pt size are plotted. The simulations do reach a statistically stationary state after 100,000 iterations, as can be seen in Figure 8, and the average cluster size occurs

for the case with BaO as expected. In addition, the cluster size distribution indicates that the BaO case has a different distribution than the case without BaO, and the presence of BaO oxide inhibits formation of large clusters.

We have implemented and tested a new rules-based NO_x chemistry module. We are in the process of performing long-timescale simulations of NO_x chemistry with coarsening. Furthermore, we are interacting with the microscopy group at the HTML of ORNL, where several experiments have been identified that would produce data that can be compared with simulation. Thus, our simulation results would assist in interpreting ongoing experimental efforts at the NTRC and HTML facilities on Pt coarsening and its effect on NO_x chemistry. Equally important, the results will be used to determine the correlation of atomistic effects to aging and efficiency that will be incorporated into the CLEERS LNT database. A key aspect of this work is that it will help bridge the gap between the microscopy experiments and translating their results through simulation into usable performance numbers and criteria.

Conclusions

Administrative Support

The CLEERS Planning Committee and LNT, DPF, and SCR Focus Groups are now fully functioning as intended and have successfully facilitated collaborations among the Diesel Crosscut Team members. ORNL, PNNL, and SNL are providing special expertise, equipment, and facilities that are not readily available otherwise to the OEM members. The CLEERS activity allows OEMs and suppliers to cooperate with each other, national labs, and universities on non-competitive issues. These types of collaborations are important for leveraging limited resources.

The seventh CLEERS workshop was held June 16 and 17 at the Detroit Diesel Corporation training facility in Detroit. All three emissions control technology areas (LNTs, DPFs, and SCR) were covered, but the greatest emphasis was on DPFs and SCR. The complete technical program, meeting summary, and most of the presentations are available on the website (www.cleers.org). This was the

largest workshop to date, with a total of 90 registrants and considerable participation from emissions controls suppliers as well as OEMs.

A key achievement has been the development of an experimental protocol for characterizing LNT materials in bench-flow reactors. This protocol is intended to provide the basis of standard kinetic 'maps' (i.e., data templates) for communicating critical simulation properties. It is anticipated that such maps will be useful to OEMs in generating LNT performance parameters for their individual user models and systems simulations. The current protocol was reached as a consensus among the LNT Focus Group with considerable interactions from collaborating supplier representatives.

Joint Development of Benchmark Kinetics

The ongoing experimental bench-reactor studies at ORNL contributed significantly to the development of the LNT characterization protocol. These experimental studies have evaluated model LNT materials fabricated locally as well as samples obtained through MECA and now commercial LNT samples from Umicore. The model and Umicore samples are currently being analyzed for their detailed chemical composition and microscopic features. Ford has also provided Toyota DPNR and LNT samples that will be included in the ORNL studies. The ORNL bench-flow reactor is undergoing extensive modifications to ensure compliance with key requirements of the draft characterization protocol. Simplified global models of LNT capture and regeneration have been completed and documented in publications and on the CLEERS website.

Micro-Scale Catalyst Modeling

A rules-based Monte Carlo code has been created that better captures the realistic particle distribution within a Pt island as well as distribution of the islands. This new approach better represents the experimentally observed behavior. Post-processing tools have been added to visualize the coarsening effects and also to track the particle size distribution with time. The code is being validated for both small-scale (10,000 cells) and large-scale systems (500,000 cells) for long timescales and compared to available experimental data.

Presentations

1. A simple limiting-case LNT model, K. Chakravarthy, Sixth Department of Energy Crosscut Workshop on Lean Emissions Reduction Simulation, GM R&D Center, Warren, Michigan, September, 2003.
2. A bench-scale study of NO_x capture in Pt/K/Al₂O₃ NSR (LNT) catalysts, K.
3. Chakravarthy, K. Lenox, S. Daw, W. Partridge, T. Miller, J.-S. Choi, DOE National Laboratory Catalysis Conference, Oak Ridge, Tennessee, October, 2003.
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7. Regeneration behavior of NO_x storage-reduction catalysts under simulated or realistic diesel exhaust, J.-S. Choi, T. Miller, W. S. Epling, S. P. Huff, K. Chakravarthy, K. E. Lenox, W. P. Partridge, C. S. Daw, 4th Department of Energy National Laboratory Catalysis Conference, Oak Ridge, Tennessee, 2003 (poster).

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1. "Phenomenology of NO_x adsorber catalysts", C. S. Daw, K. E. Lenox, K. Chakravarthy, W. E. Epling, and G. Campbell, International Journal of Chemical Reactor Engineering, Vol. 1 (A24), 2003.
2. "Global modeling of NO_x breakthrough from lean NO_x traps", K. Chakravarthy, S. Daw, T. Miller, A. Strezlec (under preparation, to be submitted to International Journal of Chemical Reactor Engineering).
3. "Adsorption isotherm based modeling of NO_x storage in lean NO_x traps", K. Chakravarthy, S. Daw, T. Miller, K. Lenox, A. Strezlec (under preparation, to be submitted to Applied Catalysis B : Environmental).
4. "Key characteristics of the sorption process in lean NO_x traps", K. Chakravarthy, C. S. Daw, K. E. Lenox, SAE 2003-01-3246, SAE Powertrain & Fluid Systems Conference & Exhibition, Pittsburgh, Pennsylvania, October, 2003.
5. "Assessing reductant chemistry during in-cylinder regeneration of diesel lean NO_x traps", Brian H. West, Shean P. Huff, James E. Parks, Sam A. Lewis, Jae-Soon Choi, William P. Partridge, and John M. Storey, SAE Technical Paper 2004-01-3023 (2004).
6. "Spatially-resolved in situ gas-phase speciation during the cyclic operation of monolithic NO_x storage-reduction catalyst based on Pt/K/Al₂O₃: comparison between H₂ and CO in regeneration step", Jae-Soon Choi, William P. Partridge, and C. Stuart Daw, Applied Catalysis A : General, to be submitted.
7. "Intra-channel evolution of carbon monoxide and its implication on the regeneration of monolithic NO_x storage-reduction catalyst based on Pt/K/Al₂O₃", Jae-Soon Choi, William P. Partridge, William S. Epling, and Neal W. Currier, in preparation.

II.B.6 Cross-Cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Diesel Particulate Filter (DPF) Modeling

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Objectives

- Develop improved modeling capabilities for diesel particulate filtration
 - Create improved models of the local properties of the soot filter, e.g., cake permeability, density, morphology
 - Develop improved sub-grid representations of the local soot oxidation reactions in diesel soot filters, e.g., oxidation mechanisms, detailed kinetics, global rates
- Coordinate and lead the CLEERS DPF sub-team activities (see www.cleers.org for sub-team minutes and updates)
 - Provide project updates to the industry sub-team, solicit feedback, and adjust work scope accordingly
 - Lead technical discussions, invite distinguished speakers, and maintain an open dialogue on DPF modeling issues
 - Lead working group formed to create a “DPF standard map”

Approach

- Map the substrate microstructure to create a computational “physical” domain
- Apply a lattice-Boltzmann flow field solution
- Incorporate soot particle motion and deposition in two manifestations
 - As a discrete particle model
 - As a continuum representation
- Incorporate soot oxidation mechanism(s)
- Validate models with experimental results
- Perform parametric analysis with the detailed model
- Develop low-dimensional sub-models from the parametric data

Accomplishments

- Full-flow single particle deposition model has been developed
- Partial differential equation based continuum soot cake model has been developed
- Employing single-channel experimental technique for model validation
- Coordinated and led monthly telecons for DPF sub-team
 - Formed a “DPF mapping” working group
 - Developed an initial “short cycle” test matrix

Future Directions

- Quantitative studies of filter performance metrics
 - Capture efficiency as a function of time/soot loading
 - Measure pressure drop as a function of time/soot loading
- Parametric studies with
 - Varying Darcy resistance for deposited particle regions
 - Adjustable capture probability
- Smaller-scale models including
 - Realistic particle size distribution
 - Complex irregular particle shapes
 - Agglomeration of moving particles
- Particle deposition with simultaneous filter regeneration
 - Incorporation of oxidation mechanism(s)

Introduction

Diesel particulate filters (DPFs) are the leading candidate technology for control of diesel engine particulate emissions. While this technology appears very promising, it is still not sufficiently mature for commercial implementation in heavy-duty trucks. Considerably more research and development will be needed to address the numerous unresolved issues [1,2,3,4]. Of particular concern is the potential for a significant degradation in fuel efficiency of diesel-powered vehicles employing DPF. This degradation is due to two inherent features of DPFs:

- They increase engine backpressure, and
- They require energy input for active regeneration.

Minimization of both of these items is linked to the fundamental properties of soot capture and oxidation on the nano/micron-length scales. It is becoming increasingly apparent that modeling and simulation are essential aspects of the needed R&D because exhaustive experimental evaluation of each possible system configuration is simply too costly and too time-consuming to be practical. In particular, both industry and DOE need access to the ability to accurately simulate trends and make objective comparisons of the various options for system materials and designs so that empirical experimentation can be minimized.

Through several technical workshops sponsored by the DOE Diesel Crosscut Team under CLEERS,

the diesel emissions control stakeholder community (including automotive and engine companies, national labs, and universities) has identified the most pressing un-addressed needs for modeling and simulation. For DPF, the modeling parameters of greatest concern are those associated with

- Local properties - cake permeability, density, morphology
- Kinetics - oxidation mechanisms, detailed kinetics, global rates
- Simple 1-D models (using the information from the first two bullets) for systems modeling
- Detailed 3-D models for understanding capture and oxidation phenomenon (for design and optimization of devices)
- Flow distribution - packing, anisotropic regenerations (for practical engineering considerations)

Of the above, the current project focuses on the first two bullets – local properties and kinetics – and how these interact with the physical distribution of particles to determine peak regeneration temperature, backpressure and capture efficiency.

Approach

A computer program has been developed to predict the nature and location of soot deposits within porous filter substrates by simulating the flight and deposition of individual soot particles. The lattice-Boltzmann method is used to solve for the flow field

of exhaust through the substrate microstructure as soot deposits form. The motion of simulated soot particles is derived from the exhaust flow field and includes random Brownian motion. Predicted soot deposits within the substrate and on the filter wall surface are being validated with various experimental approaches.

Once the fine-scale lattice-Boltzmann models are created and validated, they will be used to run parametric tests. The results of these tests will then be used to create improved sub-models (algorithms) which can be incorporated into standard device-scale DPF models.

Results

The lattice-Boltzmann method is an increasingly popular alternative to traditional computational fluid dynamics (CFD). For most CFD approaches, the three-dimensional Navier Stokes equations are discretized in time and space, and a global pressure field is solved for at each time step. With the lattice-Boltzmann method, the Boltzmann equation for local velocity probability distributions is discretized in time, space, and direction. The pressure field evolves and the Navier Stokes equations are recovered as lattice nodes relax toward equilibrium velocity distributions. For the DPF substrate model, an incompressible formulation of the lattice-Boltzmann method was used similar to that described by He and Luo [He, X. and Lou, L. S. "Lattice Boltzmann Model for the Incompressible Navier-Stokes Equation", *Journal of Statistical Physics*, Vol. 88, Nos. 3/4, 1997.].

In order to resolve the exhaust flow field and particle capture mechanisms at the scale of individual pores, it was first necessary to construct an accurate three-dimensional map of a DPF substrate microstructure. A Corning EX-80 filter was sectioned to provide several 1-cm samples of the substrate wall, which were potted in an acrylic epoxy microscope mount. The samples were then ground to the filter wall surface and polished flat. An automatic polishing station was used to remove additional material in approximately 6-micron increments. After each 6-micron layer was removed, a micrograph was taken of the sample. This procedure of polishing and imaging was repeated 25 times and produced a series of 25 surface images of

the porous filter wall structure. The images were then processed with image analysis software and converted into digital representations of the solid filter material and void space. Once a physical domain was created, the lattice-Boltzmann technique was applied to simulate the exhaust flow field.

The formation of soot deposits has been simulated by the motion and capture of individual particles in the work of Konstandopoulos and others [Konstandopoulos, A.G. "Deposit Growth Dynamics: Particle Sticking and Scattering Phenomenon", *Powder Technology*, 109, pp. 262-277, 2000. Konstandopoulos, A.G., Saperdas, E., and Masoudi, M. "Microstructural Properties of Soot Deposits in Diesel Particulate Traps", *SAE Technical Paper Series*, 2002-01-1015.]. Aggregate particles in these models were represented as mono-sized spheres with an aerodynamic diameter of 100 nm. The soot particles in this approach moved in a linear trajectory and either rebounded or were captured upon impact. The effect of the fluid motion on that of the particles was not included directly. Since particles could not be carried around corners by the flowing fluid, applicability to the depth filtration mode was limited. The work described here represents an effort to extend this type of modeling approach by adding the effects of the flowing exhaust on soot particle motion.

For the sake of simplicity and easy comparison with previous models, soot particles in the lattice-Boltzmann model were considered to have a single aerodynamic diameter of 100 nm. Future work will examine the effects of particle size distributions on filter behavior. Particles with an aerodynamic diameter of 100 nm are essentially inertia-less at the time and length scales examined. For larger aggregates, however, particle momentum may become significant, in which case particle acceleration must be calculated from drag forces.

Local fluid velocities are estimated from the eight surrounding lattice sites using tri-linear interpolation. Each particle is then displaced in the direction of this average velocity according to the particle time step. A particle time step of 3×10^{-7} seconds was used for this initial study.

Brownian motion is super-imposed on the motion caused by the local average fluid velocity. The

average magnitude of random Brownian motion determines the particle diffusivity, which is calculated according to

$$D_p = \frac{k_B \cdot T}{3\pi \cdot \mu \cdot d_{particle}} \cdot \left(1 + Kn \left(1.257 + 0.4e^{1.1/Kn} \right) \right)$$

where k_B is Boltzmann's constant, T is the absolute exhaust temperature, μ is the dynamic fluid viscosity, $d_{particle}$ is the aerodynamic diameter, and Kn is the Knudsen number calculated as

$$Kn = \frac{2\lambda}{d_{particle}}$$

where λ is the exhaust mean free path [5].

A perfectly inertia-less particle with no Brownian motion would follow the fluid through the filter substrate and would be unlikely to touch the solid walls. Inertial deposition is important for large particles, wherein the particle's momentum causes it to skid between curving streamlines and thus increases its likelihood of contact with obstructions. For smaller particles, Brownian motion becomes the important effect by bouncing the particles between streamlines and allowing them to interact with the solid substrate walls.

For simplicity, and to reduce the number of particle motion calculations, particles were dealt with in "clouds" or "bundles" having a diameter of 1 micron. The individual bundles can have any aerodynamic diameter and can therefore behave as agglomerates of any specified size with respect to momentum and Brownian motion. The 1 micron diameter is used only to test for contact with the solid substrate regions or previously deposited particles. Since the controlling substrate pores can have diameters of many tens of microns, the bundle approach allows soot deposit shapes to be sufficiently resolved with a tractable number of particle motion calculations.

Particles are assumed to be deposited immediately upon contact with solid substrate walls or with previously deposited particles. The resistance of soot deposits to exhaust flow is modeled by assigning deposited particles to the nearest lattice site. Resistance to flow through that lattice site is then included as an additional Darcy force term in the lattice-Boltzmann solution. The Darcy resistance at a lattice site is incrementally increased as more

particles deposit near it, or in other words as the porosity of the soot deposit in that lattice volume decreases. The current discrete particle model does not consider passive regeneration, re-entrainment, or mechanical restructuring of the soot deposits as they form.

Table 1 lists conditions modeled for the simulation results shown here. Almost a million particle bundles were introduced during the model run, 98.5% of which were captured by the filter.

Table 1. Parameters for Model Run

Wall flow velocity	3.6 cm/s
Particulate concentration	0.02 g/scm
Exhaust temperature	300°C
Loading time modeled	3.3 hours

Figure 1 shows a cross-section of the filter wall as the soot deposits form. Solid substrate regions are shown in white and soot deposits in black. Note the extent of depth filtration in the early stages of loading. Bottlenecks in the pore structure within the substrate wall quickly become blocked by soot deposits. As pores near the surface become blocked, growth of deposits deeper within the substrate slows and then stops. The total loading at the end of the simulation would correspond to about 3.9 g/m² of filter area. A Corning EX-80 5.66 x 6 inch cordierite

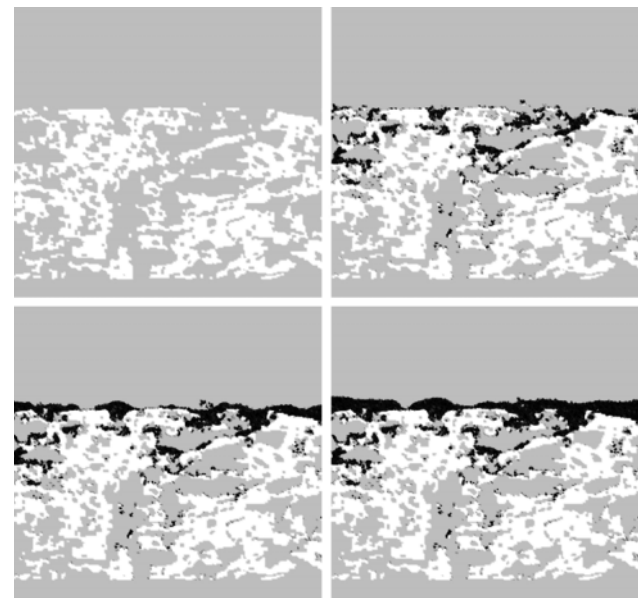


Figure 1. Cross Section of Filter during Loading Shown at Time = 0, 66, 132, and 198 Minutes

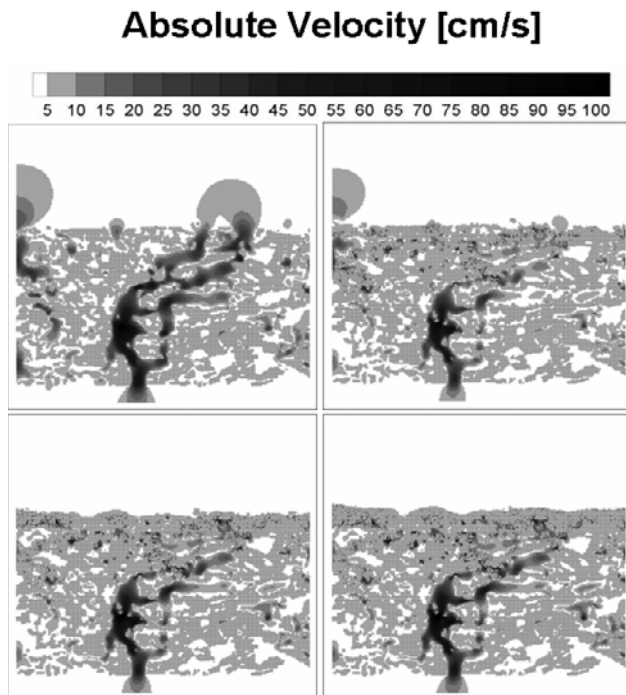


Figure 2. Cross Section of Filter Showing Absolute Velocity at Time = 0, 66, 132, and 198 Minutes

filter has a filtration area of 1.66 m^2 and a maximum soot loading of roughly 15 g [8]. For this filter, the end of the simulation would correspond to about 6.5 g of total loading or 43% of capacity.

Figure 2 shows exhaust velocity contours at the same cross-section over the same time period. Solid substrate regions are shown in a mesh pattern. Exhaust velocity near the surface of the clean substrate is highly non-uniform, with high velocities near the entrances to important flow paths and stagnation regions elsewhere. Since the soot aggregates modeled are inertia-less, they are all swept into these flow paths and have opportunities to deposit anywhere along the exhaust routes through the filter material. The formation of deposits in key bottlenecks quickly begins to redistribute the flow near the surface. Even after surface deposits begin to form, the exhaust velocity is still greater over the entrances to important flow paths. This results in mounds of soot forming over large pores while some locations on the substrate wall are still bare. Eventually, the accumulating soot distributes the exhaust flow evenly over the deposit surfaces, and the few remaining stagnation areas shrink as the

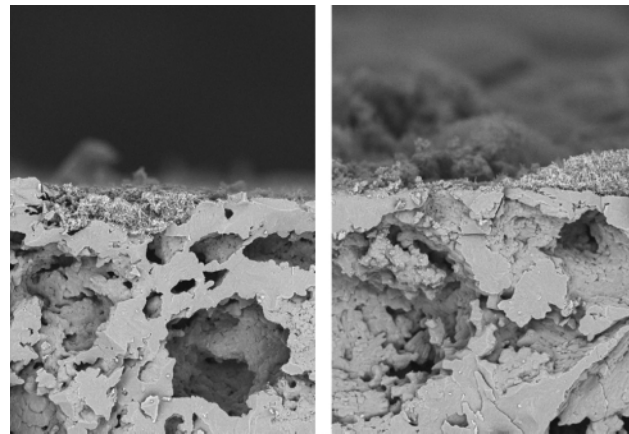


Figure 3. Scanning Electron Micrographs of Soot Deposits

deposits grow and blend together. Flow patterns deep within the substrate are relatively unaffected by the degree of soot loading.

Several qualitative similarities can be observed between real soot deposits and those predicted by the model. Figure 3 shows pictures of actual soot deposits near the surface during early stages of loading. The micrographs show examples of shallow pore mouths at the substrate surface filling with soot while other areas on the surface remain bare. As loading progresses, mounds of soot tend to form in some locations. Sizable soot deposits are occasionally seen deep within the substrate wall, as shown in Figure 4, but most of the void space within the substrate is clear of soot, even after a significant layer has formed on the surface.

Conclusions

Discrete particle modeling with realistic flow field effects is providing insight into the way soot deposits form with respect to substrate microstructure. Soot deposits predicted by the simulation have been found to share many qualitative features with those observed in real filter substrates. Quantitative validation of the model is in progress using a variety of approaches. Improving the fidelity of the model by adding effects such as the aerodynamic size distribution of real soot particles could lead to accurate predictions of pressure drop versus soot loading for new or hypothetical substrate microstructures.

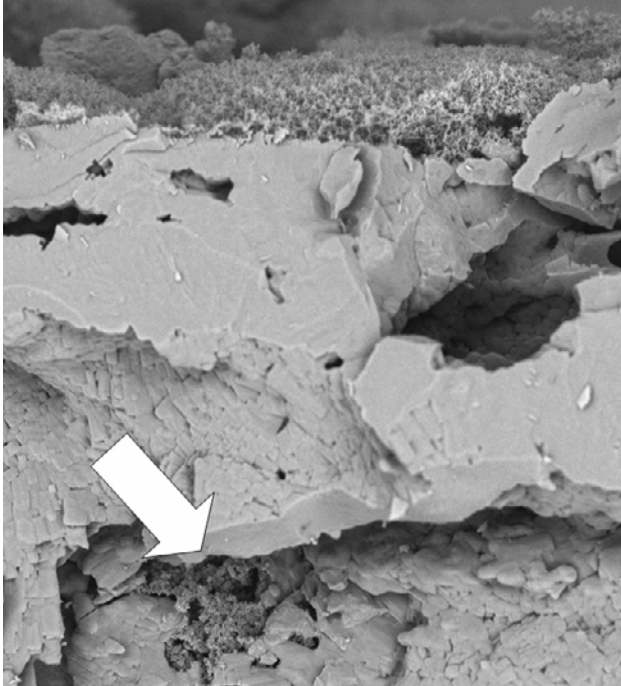


Figure 4. Micrograph Showing Soot Deposit Within Substrate Wall

To date, the lattice-Boltzmann method has been found to be:

- versatile and easy to use
- proven effective for extruded ceramic structures with tortuous pores
- able to qualitatively reproduce several structural features of soot deposition
- easily implemented with incremental improvements
- able to address macroscopic phenomena such as particulate capture efficiency and pressure drop
- supportive of continuum modeling of the soot layer

Special Recognitions & Awards/Patents Issued

1. The paper SAE 2003-01-0835 was selected for inclusion into SAE Transactions.

2004 Publications/Presentations

1. G. Muntean, D. Rector, D. Herling, D. Lessor and M. Khaleel, "Lattice-Boltzmann Diesel Particulate Filter Sub-Grid Modeling – a progress report", SAE 2003-01-0835, February, 2003.

2. G. Muntean, "CLEERS DPF SUBTEAM", presented at the CLEERS workshop, September 2003.
3. G. Muntean, D. Rector, and D. Lessor, "Modeling Diesel Soot Filtration at the Smallest Length Scales: A Lattice-Boltzmann Approach", presentation at the American Filtration Society conference, September 2003.
4. G. Muntean, and M. Stewart, "Characterization of Cordierite Substrates for Particulate Filtration Using Lattice Boltzmann Techniques and Experimental Measurements", presentation at the American Ceramics Society conference, January 2004.
5. G. Muntean, "CLEERS DPF Sub-team Update", presented to the diesel crosscut team, March 2004.
6. G. Muntean, M. Stewart, and G. Maupin, "CLEERS DPF Modeling", presentation at the DOE Combustion and Emission Control Review, May 2004.
7. M. Stewart, "Discrete Particle Modeling of Diesel Soot Filtration", presented at the CLEERS workshop, September 2004.

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II.B.7 Advanced CIDI Emission Control System Development

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DOE Technology Development Manager: Ken Howden

Subcontractors:

FEV Engine Technology, Inc., Auburn Hills, MI

ExxonMobil Research and Engineering Company (EMRE), Paulsboro, NJ

Objective

- Develop and demonstrate a highly efficient exhaust emission control system for light-duty compression ignition direct injection (CIDI) engines to meet 2007 Tier 2 emissions standards (0.07 g/mi NO_x, 0.01 g/mi PM [particulate matter]) with minimal fuel economy penalty and 120,000 mile durability.

Approach

- Conduct parallel engine dynamometer and vehicle testing.
- Continue research to identify the most active and durable catalysts and catalytic diesel particulate filters (CDPFs).
- Continue research to determine the most selective and durable exhaust gas sensors.
- Use a very low-sulfur diesel fuel to represent U.S. fuel of 2007 and beyond.
- Assist in the development of a feasible aqueous urea delivery system for diesel vehicles.

Accomplishments

- Low-mileage Tier 2 Bin 5 standards were achieved using a fresh catalyst system of oxidation catalysts, urea selective catalytic reduction (SCR) and CDPF in a mid-sized diesel prototype engine designed for a light-duty truck. Engine-out NO_x was lowered by 40% through the use of a cooled, low-pressure exhaust gas recirculation (EGR) system. An additional 90% reduction of NO_x by the urea SCR system resulted in a tailpipe NO_x level of 0.04 g/mi.
- A rapid warm-up procedure was developed for use during the cold-start portion of the Federal Test Procedure for light-duty vehicles (FTP-75), decreasing the time for the urea SCR system to begin operating at high efficiency by almost a minute. Fuel economy was reduced by less than 1%.
- Hydrocarbons (HC) and carbon monoxide (CO) were converted at or above 97% cycle efficiency, resulting in 0.08 g/mi HC and 0.3 g/mi CO.
- Improvements were made to the durability of the urea SCR system, including modifications to the urea dosing system to eliminate clogging. The SCR catalyst was improved for greater thermal durability to withstand CDPF regeneration conditions.
- A separate vehicle equipped with a urea SCR system maintained 80% FTP-75 NO_x conversion after 35,000 miles of on-road driving. Due to limited access to engine calibration, there was no rapid warm-up procedure; therefore, 80% was the maximum NO_x conversion expected.
- A co-fueling dispenser for urea and diesel fuel was tested successfully to minus 20°F. Heaters were used in the urea tank and delivery system to prevent freezing. A potential nozzle durability issue was discovered that caused leakage of aqueous urea into the diesel fuel line.

- The economics of an aqueous urea infrastructure for light-duty (LD) service stations in the U.S. was studied. The cost of co-fueled urea was high in the short-term during introduction and was greatly dependent on the number of LD diesel vehicles that would require urea.

Future Directions

- Begin durability testing of the emission control system on the engine dynamometer.
- Continue laboratory testing of improved SCR catalyst formulations.
- Continue laboratory and vehicle testing of NO_x sensors, with the aim of developing a better model of their response.
- Continue laboratory testing/development of ammonia sensing technologies and determination of their value in a urea SCR diesel aftertreatment system.
- With a major nozzle supplier, improve the durability of the co-fueling nozzle to prevent leakage of aqueous urea into the diesel fuel line.

Introduction

Particulate matter (PM) and NO_x emissions are primary concerns for diesel vehicles required to meet 2007 Federal Tier 2 and California LEVII emission standards (Table 1). These standards represent a 90-95% reduction from current Federal Tier I diesel standards.

Table 1. 2007 Emission Standards* (passenger cars and light-duty vehicles)

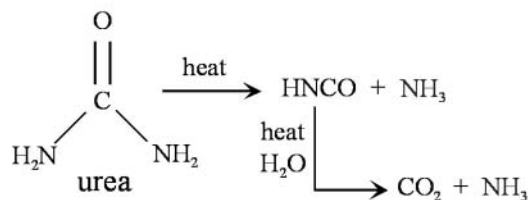
Standard (g/mi)	50,000 miles		120,000 miles	
	NO _x	PM	NO _x	PM
California LEVII	0.05	----	0.07	0.01
Federal Tier 2, Bin 5	0.05	----	0.07	0.01

*Supplemental Federal Test Procedure standards not included.

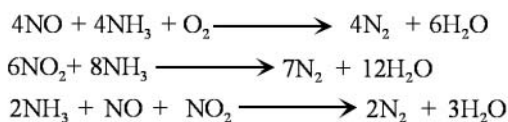
The high oxygen content of diesel exhaust makes onboard NO_x control complicated. The available technologies for high NO_x reduction in lean environments include selective catalytic reduction (SCR), in which NO_x is continuously removed through active reductant injection over a catalyst; and lean NO_x traps (LNT), which are materials that adsorb NO_x under lean conditions and require periodic regeneration under rich conditions to reduce NO_x to N₂. The technology with the most potential to achieve 90+% NO_x conversion with minimal or no fuel economy penalty is SCR with an ammonia-based reductant such as aqueous urea. Ammonia-SCR has been used extensively for stationary source

NO_x control [1]. Its high selectivity and reactivity with NO_x in high-O₂ environments makes SCR attractive for diesel vehicle use. The main reactions are shown below:

urea decomposition:



NO_x reduction:



Compared to ammonia, aqueous urea is much safer for onboard vehicle use. Feasibility has been proven by past work at Ford [2,3], Volkswagen [4], Mack Truck [5] and DaimlerChrysler [6].

Control of diesel PM is accomplished with a periodically regenerated ceramic filter. The filter may be washcoated with precious metal to help oxidize HC and collected soot. A diesel oxidation catalyst (DOC) may also be placed upstream of the filter to further aid in filter regeneration.

Approach

At Ford, supplier catalysts were tested in a laboratory flow reactor and ranked for fresh and aged

conversion levels. Full-size monoliths of the most promising formulations were installed in the engine dynamometer and onboard the vehicle and tested in parallel. Modeling was used to help choose the catalyst configuration with the highest potential to meet the emission standards. Since cold-start plays an important role in emission control system functionality, special emphasis was placed on rapid warm-up strategies. Appropriate exhaust gas sensors and control strategies were used for durable system function. The economics of delivering aqueous urea to LD diesel vehicles was explored.

A 14,000 gallon batch of ultra low sulfur (<15 ppm S) diesel was manufactured for use in the optimization and long-term durability portions of the project. Fuel properties were selected to approximate the product quality anticipated in the 2006 market. The resultant fuel also met the Environmental Protection Agency (EPA) certification fuel standards for 2007.

Results

Over 90% NO_x conversion was achieved with fresh catalysts on a simulated FTP-75 on the engine dynamometer. The urea injector was pointed against the exhaust flow. A spray target, developed for this program at FEV, was added to the system, resulting in enhanced mixing of reductant in the exhaust gas. Engine-out NO_x was reduced approximately 40% through the use of higher EGR levels. A rapid warm-up procedure was used during the cold-start portion of the test cycle. Tailpipe emissions and system efficiencies from four simulated FTP-75 tests were averaged, as shown in Figure 1. Emissions of THC (total hydrocarbon) were below the non-methane standard. Tailpipe NO_x was below the Tier 2 Bin 5 (120,000 mile) level of 0.07 g/mi NO_x, and PM levels were approximately 1 mg/mi.

Several improvements were made to the SCR system for more durable conversion of NO_x. The urea dosing system clogged due to collection of solid urea in the urea/air mixing chamber located downstream of the urea injector. A new design eliminated any dead volume that might collect urea. The system was tested successfully for 10,000 miles on a 2.4L European Ford Transit, with no need for interim cleaning of the mixing chamber, transfer tube or nozzle.

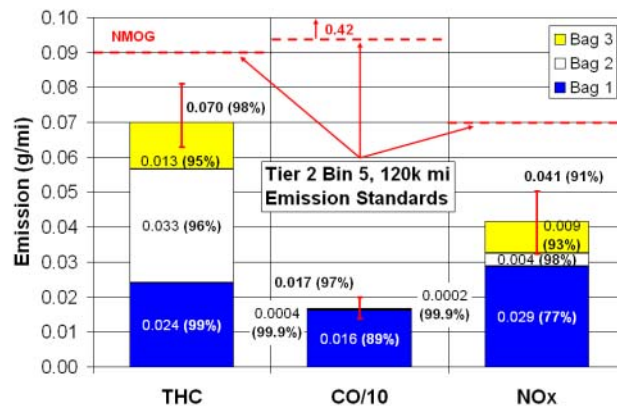


Figure 1. Average tailpipe emissions and system efficiencies from four cold-start FTP-75 simulations with fresh catalysts on the engine dynamometer. Enhanced mixing of reductant in the exhaust gas and additional EGR resulted in a low mileage tailpipe NO_x level below Tier 2 Bin 5. THC results are shown while the standard does not include methane (NMOG).

The thermal durability of the SCR catalyst was tested extensively in the laboratory because it will be exposed to high temperatures during regeneration of the CDPF. Catalyst cores were aged at high temperature for 20 h in 14% O₂, 4.5% H₂O, 5% CO₂, balance N₂, at 30k h⁻¹. Sulfur was not added because low sulfur diesel fuel was assumed. High NO_x conversion was maintained over a wide window after aging at 700, 725 and 750°C. A significant drop in performance occurred after aging at 800°C when the feedgas NO_x consisted mainly of NO. As the amount of NO₂ relative to NO in the feedgas was increased, the performance improved. These results indicated that the SCR catalyst should be able to withstand exposure to high temperatures during CDPF regenerations, especially if the upstream oxidation catalyst retains high activity for NO₂ production.

Both NO_x and NH₃ sensors were studied in the laboratory and onboard the project vehicle. A pre-production NO_x sensor was used upstream of the underbody oxidation catalyst to ensure that the correct amount of urea solution was injected during transient operation. Several prototype NH₃ sensors were tested downstream of the SCR catalyst to monitor NH₃ slip for possible feedback control of urea dosing. Laboratory tests demonstrated good sensitivity to NH₃ with some sensitivity to H₂O.



Figure 2. Prototype Co-Fueling Dispenser

Making the use of urea completely transparent to the customer would facilitate introduction. A way to do this is through the use of a concentric nozzle that "co-fuels" urea and diesel fuel simultaneously [7]. A prototype dispenser was fabricated using a modern diesel dispenser and off-the-shelf parts as shown in Figure 2. The dispenser was successfully tested to minus 20°F with heating where necessary. Durability testing of the nozzle indicated a small, intermittent leak of urea (0.5%) into the fuel within the nozzle/insert seal.

An economics study was conducted to understand the costs associated with providing aqueous urea to LD diesel vehicle customers. Model inputs were derived from existing data when possible. The number of service stations used in the model matched the current number of about 167,571 stations in the U.S., with approximately 1/3 selling diesel fuel. Trends in LD diesel vehicle population growth and fuel consumption were derived from DOE's Energy Information Administration 2003

Annual Energy Outlook [8], and vehicle distribution and mileage accumulation by age came from EPA's MOBILE6 model [9]. It was assumed that a solution of 32.5 wt% urea in deionized water would have a wide usage among heavy-duty (HD) diesel vehicles with an established pathway from the manufacturing plant to distribution facilities. The capital payout period for the investment in co-fueling dispensers was assumed to be three years, at a 15% rate of return. The urea consumption was estimated to be 2% of the diesel fuel consumption on average. Results did not include profit markup or taxes, and all estimates were in constant dollars.

The estimated cost of aqueous urea to the customer at the service station was calculated by the following equation:

$$\text{Estimated Urea Cost at the Service Station (\$/gal)} = (\text{Manufacture} + \text{Distribution Cost}) + \text{Storage Cost} + \text{Delivery Cost} + \text{Service Station Cost.}$$

The estimated urea cost, not including service station costs, was found to be about \$1.20/gal.

Service station costs included the capital investment and operating expenses divided by the urea volume throughput for that station. The capital cost of a single co-fueling dispenser was estimated to be about \$26,500, and the annual operating expenses, with full heating in winter, were calculated to be about \$1,777/yr. The resulting cost for co-fueled urea was therefore highly dependent on the number of dispensers installed and the urea demand.

The lowest-cost scenario for an aqueous urea infrastructure was determined to be the use of bottled urea during the introduction of urea SCR vehicles in 2007, with co-fueling dispensers preferentially installed at the highest-throughput light-duty diesel stations as demand for urea increases. The cost of bottled urea was estimated at \$3.66/gal. For 2010, it was estimated that co-fueled urea would be cost-competitive with bottled urea if installed at the top 1% of service stations (based on volume throughput of diesel fuel). After the cost recovery period, the long-term cost of co-fueled urea was about \$1.50/gal.

Conclusions

- The objective of emissions reduction to 0.07 g/mi NO_x and 0.01 g/mi PM based on engine

dynamometer testing over the FTP drive cycle was met with a fresh emission control system of urea SCR and CDPF. System improvements were required to lower engine-out NO_x and enable rapid exhaust system warm-up.

- Durability of the urea dosing system was improved after redesign of the mixing chamber.
- In the laboratory flow reactor, the SCR catalyst withstood temperatures in excess of those typically associated with CDPF regeneration, and NO_x conversion was high assuming the upstream oxidation catalyst had high activity for NO₂ production.
- Laboratory and in-vehicle testing of pre-production NO_x and prototype NH₃ sensors was successful.
- A co-fueling dispenser for urea and diesel fuel was tested successfully to minus 20°F, and a potential nozzle durability issue was discovered.
- The cost of co-fueled aqueous urea for LD diesel vehicles is projected to be high in the short-term during introduction. Costs are minimized when bottled urea is used initially and co-fueling is phased in gradually. The long-term cost of co-fueled aqueous urea is estimated to be \$1.50/gal.

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