The Eighths CLEERS workshop was hosted by University of Michigan at their Professional Education Center.

About 120 people attended the workshop with the following breakdown:
2% Software companies
15% Universities
18% Emission Control suppliers
28% Automotive and Engine manufacturers
21% National Laboratories and Government
16% Consulting companies

Day1 – DPF and DPNR

Randy Vander Wal gave a presentation on measurement of the nanostructure of soot using transmission electron microscopy (TEM). Soot nanostructure refers specifically to details in the carbon lamella length, orientation, separation and tortuosity. This nanostructure appears to be highly variable; depending on the temperature, residence time and fuel conditions under which the soot was produced. To quantify differences in nanostructure, Randy employed a lattice fringe analysis program developed by NASA to analyze HRTEM images. Oxidation rates are dependent upon nanostructure; therefore nanostructure can be used to correlate soot oxidation properties. The latter is one of the key issues associated with simulating DPF regeneration.

Kyeong Lee showed results of morphological and microstructural investigations of diesel particulates. Experimental setup and techniques used at ANL (thermophoretic sampling and TEM) enabled him to study important properties of particulates. Particulate morphology is strongly affected by engine operating conditions. Size and disorder of crystal structures are found to be sensitive to temperature while engine speed was relatively less important for particle growth. Effects of exhaust components on soot particles were also investigated. Clear morphological changes were observed in particulates as they are transported along the exhaust pipe.

Katsunori Hanamura gave a presentation on reaction of diesel particulates during regeneration of DPF. Observations at both macroscopic and microscopic levels were given, and revealed interesting details of the trapping and regeneration processes. Reaction mechanisms were described by a reaction diagram using the inlet gas temperature and the particulate mass. From microscopic observation, it is concluded that the localized heterogeneous ignition events initiate the regeneration process.

Athanasios Konstandopoulos addressed the current state of knowledge on DPF Systems drawing from his recent work in the field. His central thesis was that a more detailed description of the coupled transport, structural and reaction micro-phenomena occurring at the filter wall and pore scales is indispensable. He also argued that the best modeling approach combines experimental and computational methodologies, starting from well-defined experiments with small scale filters under realistic exhaust conditions. Ultimately, full scale tests of the integrated emission control system with modern diesel engines are needed over steady state and transient conditions. Prof. Konstandopoulos finalized his discussion with a call for more collaborative work to establish standards and recommended practices for modern DPF systems.

Dave Foster presented results of DPF studies in the University of Wisconsin. Detailed analysis of exhaust gases, particulate matter and performance of DPF (Corning EX 80/17) under different operating conditions were presented. Three modes of engine operation were used for analysis: mode 3 (medium load and high speed), mode 4 (low load and high speed) and mode 5 (high load medium speed). Particle composition and distribution, effect of temperature, furnace and burner regenerations were presented for each of these modes.

Andrea Strzelec presented experimental plan to develop DPF maps. There is a need to develop standard test procedures for determining the oxidation rates for soot in a DPF. This information is crucial to develop engine control strategies for DPF regeneration. The CLEERS DPF focus group is utilizing components of this plan for developing a standardized DPF test protocol.

Mark Stewart gave a presentation on the progress and current challenges in micro-scale modeling of DPF. Specifically, Mark and his colleagues at PNNL are exploring the effects of pore size and shape on filtration performance. Although it is quite fundamental, such modeling is intended to ultimately lead to improvements in device-scale DPF models. Quantifying the roles of pore-scale mechanisms is necessary for improved parametric values in lower order device-scale models. Depth of soot penetration into substrate is important for several possible regeneration mechanisms. Location of soot and areas of highest oxidation rates may determine the ultimate fate of ash. Understanding the role of substrate microstructure in filtration and regeneration could lead to more optimized filter materials.

Chris Depcik presented fully transient one-dimensional based DPF model including catalytic surface reactions. His model includes propagation of chemical species and particulates. It incorporates catalyzed reactions and surface gas species equation. Fully transient capability was incorporated into model which allows the model to capture surface intermediate chemistry effects. Chris compared example results for incompressible and compressible flows to illustrate when compressibility needs to be considered.

Mohammed Hasan presented a summary of the MTU 1-D 2-layer model to simulate a Johnson Matthey Catalyzed Continuously Regenerating Trap (CCRT). The CCRT consists of diesel oxidation catalyst (DOC) upstream of catalyzed particulate filter (CPF). Data from CCRT experiment was used to calibrate the CPF model to study the filtration, loading and oxidation characteristics of the CCRT.

Alan Mueller gave presentation on a general approach for modeling DPF systems being utilized by CD-Adapco for their Star CD software package. Their model is highly comprehensive and includes, flow characteristics in individual monolith channels, global flow characteristics upstream/downstream of monolith, detailed chemical kinetics (including catalytic surface reactions and gas phase chemistry), conjugate heat transfer for the entire system, and detailed simulation of soot cake formation and regeneration. After providing example outputs for DPF test cases, Al also suggested that collaborations among the aftertreatment community should include the following:

- Agreement on standard of "ideal" laboratory tests of filters that include loading only, loading and continuous regeneration, and forced regeneration
- Agreement on standard models that can be used to characterize DPF's based on the above tests
- Utilization of the above laboratory data and model fits by vendors to characterize their products

Bob Weber presented results of a study designed to comprehensively explore the future of heavy-duty powertrains. This study gathers best available information along with detailed engine, emission control, and vehicle simulations and tries to project future trends in the development of engines, transmissions, emissions controls and fuels to meet upcoming regulations and customer demands. Implications of HCCI engines, hybrid powertrains and advanced transmissions for emission controls of the future were discussed. One particularly prominent result of Bob's recent analyses is that aftertreatment may become much less important as more advanced engine systems (e.g., those using HCCI combustion) become more available.

Naeim Henein gave a presentation on the engine control strategies needed for the efficient operation of the after treatment devices under different combustion regimes, including the conventional and low temperature combustion concept (LTC) reaching the smokeless, NOxless operation. The developed strategies are based on an experimental investigation of combustion and emissions in a small bore high speed single-cylinder research diesel engine under different operating conditions.

<u>Day2- LNT Presentations</u>

Chuck Schenk (EPA) provided an invited summary of his recent LNT studies. He concluded that results to date still support the adoption of LNT's as a viable technological option for NOx control, in spite of concerns regarding durability and sulfur tolerance. Chuck believes that adsorber formulations have significantly improved in the past 5 years; especially in regard to thermal stability and regeneration from sulfur-based deactivation.

Richard Blint (GM) presented a global kinetic model for LNT's containing barium and potassium. The basic model was constructed in collaboration with Louise Olssen at Chalmers University. Parameters for the model were determined from bench flow reactor experiments. One reaction step for each storage material (Ba and K) was used in the model. A shrinking core formulation was also used for describing the variation in mass-transfer for each of the storage components. The model was able to describe the experimental features very well, and the results show that the model can describe multi-adsorber lean NOx traps in a broad temperature range.

Chuck Peden (PNNL) showed recent results of NOx adsorbers studies at PNNL. PNNL studies are addressing details of the elementary adsorption, reaction and desorption processes, as well as the identity of reaction intermediates and their thermal stabilities on the catalyst surfaces. It is expected that these detailed measurements will be able to supplement the information coming from the standard protocol to clarify some of the critical reaction limiting steps during NOx capture and regeneration.

Todd Toops (ORNL) presented results of ORNL studies of LNT deactivation due to poisoning agents (phosphorus and sulfur) and thermal aging. Sulfur/phosphorus poisoned catalyst can be recovered while thermal affects are unrecoverable loss. Thermal aging is primary mechanism for LNT deactivation. Todd described rapid aging and poisoning protocols that have been developed to assess the relative susceptibility of different LNT materials to these effects. Other key observations from studies with these protocols are:

- During desulfation, surface sulfates are removed quickly but bulk sulfates linger;
- H_2S and $SO_2$are not the only desulfation products;
- Moderate desulfation is the key to LNT longevity.

Jae-Soon Choi (ORNL) presented results from a bench study of LNT NOx regeneration: Specifically, Jae-Soon studied the regeneration of a $K/Pt/Al_2O_3$ LNT material using different reductants (CO and H_2). Details of the regeneration processes inside a sample monolith core were measured using the SpaciMS method developed at ORNL. Pure H_2, mixtures of CO/H_2, and pure CO had similar regeneration efficiency at 300C, but pure H_2 was clearly a better reductant at 200C. Jae-Soon has conjectured that the difference between H_2 and CO at the lower temperature is the result of CO poisoning of the Pt surface. CO conversion to H_2 by the water-gas-shift reaction appears limited and does not seem to be a major factor.

Owen Bailey (Umicore) presented an invited overview of the status of LNT formulation development from the perspective of an emissions control supplier. Using example analyses of two commercial LNT materials, Owen emphasized that there is still a compositional and architectural diversity that in some ways parallels that of advanced Pt/Rh TWC formulations. Like TWC formulations, current LNT's also incorporate relatively high levels of oxygen storage capacity based on cerium and zirconium inclusion in the washcoat. While these thermally stabilized solid solutions enhance NOx reduction, they also increase the fuel economy penalty associated with regeneration. Owen proposed that LNT modelers are going to be highly challenged to simulate and explain the effects of the significant formulation and architecture variations among commercial LNT materials, as well as explain the different transformations associated with aging.

Stuart Daw(ORNL) presented a joint discussion from ORNL and Ford (John Hoard) regarding their experience in implementing the CLEERS LNT characterization protocol. Ford evaluated the consistency of the results obtained for the Umicore reference LNT material in independent evaluations made at several different labs. Most of the discrepancies in reported measurements occurred at temperatures <=250C and >=400C.

For now Ford has concluded that it is not possible to reliably compare bench characterization from different labs. It is also unlikely that published data from different sources can be directly compared. This underscores the need to develop a truly standard set of testing conditions that can be used collectively by the LNT community. Based on ORNL's experience with the draft LNT protocol, it is clear that there are several remaining issues to be resolved before the complete objectives of the LNT Focus group have been met. Specific remaining issues include direct measurements of oxygen storage, accounting for sample length effects, inclusion of gas analysis instrumentation response, consistent reduction of degreened samples (sample stability, handling), and integration of the current performance characterization measurements with the rapid aging protocol.

Bill Epling (Cummins) gave an invited presentation summarizing the experience that Cummins has had with the current draft LNT characterization protocol. Cummins has probably had more experience with the LNT protocol than any of the other diesel CLEERS companies to date. Bill pointed out several key features that they had observed for the Umicore reference material that would be relevant for validating LNT kinetics models. He also noted several shortcomings of the existing protocol condition ranges that could be improved. These are being incorporated in an updated edition of the LNT protocol, which will be distributed to the LNT Focus Group later this summer. Bill suggested that future studies of detailed LNT kinetics should include the following measurements:

- More direct tracking of N by using simulated exhaust with non-N balance gas (e.g., Ar);
- More measurements of surface oxygen-hydrocarbon interactions (e.g., oxygen storage and hydrocarbon reforming); and
- Detailed tracking of thermal fronts in the reactor.

Chaitanya Narula gave presentation on structural changes in LNT materials due to different type of aging: flow-reactor aging, dyno aging and passenger vehicle aging. Lean and rich aged samples showed sintering of Pt particles, and migration of Ba into ceria-zirconia layer which reduces platinum-barium oxide surface area. Stoichiometric aging leads to the migration of barium into ceria- zirconia layer but the sintering of platinum is less severe. Dyno-aged samples show similar trends. Vehicle-aged samples showed the precious metal sintering occurred in the early stages of vehicle aging. Theoretical explanations of experimental data were given.

Larry Allard gave a presentation on various types of electron microscopy, and how these can be used to observe microstructural changes of LNT due to aging. Analyses so far have indicated that the bulk of precious metal sintering occurs in the early stage of LNT operation. Larry also showed example results for two reference LNT materials and one DPF filter material that have been donated to CLEERS. The first LNT material came from the Umicore GDI reference sample (donated by Owen Bailey) that is being extensively studied by the LNT Focus Group and the second LNT material is from the pre-LNT section of a DPF from a Toyota Avensis (donated by Ford). The two LNT samples show significant differences in construction and formulation relative to each other. The construction of the DPF filter material is also considerably different from the

LNT samples. Larry suggests that different approaches may be needed to characterize the microstructure in these materials because of the significant differences.

Jim Parks presented results from recent LNT regeneration studies at ORNL. The results reported were for an LNT candidate material provided through MECA. While both engine and bench reactor characterizations have been made for this material, it has not been possible to do more detailed chemical and microscopic analyses of this material because of proprietary agreements (this material is not commercially sold). Nevertheless, the extensive engine and bench tests have revealed important correlations between the two types of data and provided additional input to the development of the LNT characterization protocol as well as the understanding of potential strategies for using in-cylinder fuel modulation to control regeneration. Regarding the latter, three different regeneration strategies have been compared: So far, it appears the relatively high levels of hydrogen can be created in cylinder with certain strategies, and the level of hydrogen is probably the biggest factor in regeneration efficiency (i.e., higher is better). These studies have also revealed that over dosing of reductant during regeneration can produce large amounts (100's of ppm) of NH3 and N2O. These findings appear to be consistent between the bench reactor and engine.

<u>Day 3-Urea and HC SCR</u>
Oliver Kroecher (Paul Scherrer Institute) gave a presentation on zeolite SCR catalysts. Structure, preparation and advantages of zeolite catalysts were presented. Vanadia-based SCR catalysts are only suitable for low and intermediate temperatures; at higher temperatures a lot of byproducts are formed. Zeolites are found to be an interesting alternative to the established vanadia-based SCR catalysts. Catalytic investigations were done on Fe-, Cu-ZSM5 and vanadia-based monoliths, and their performance were compared. Cu-ZSM5 is found to be very active in reducing NOx at temperatures less than 300C; Fe-ZSM5 at T>550C and vanadia-based at intermediate temperatures. At high temperatures zeolites showed no N2O formation unlike vanadia-based one. Fe-performs better than Cu-ZSM5, and it is well suited for SCR. Thermal and hydrothermal stability of Fe-ZSM5 was presented. Fe- is found to be thermally stable catalyst, and it is resistant to sulphur. Results of ammonia adsorption experiments on Fe- were also presented.

Christine Lambert (Ford) gave update on Ford/DOE SCR program. Ford is in its third phase (Durability phase) of the program to achieve Tier 2 emission standards for 2007 using low sulfur diesel fuel as an enabler for a high efficiency aftertreatment system. Tier 2 Bin 5 standards represent 90-95% NOx and PM reduction from today's standards for diesels. Catalyzed filter was chosen for PM control; Lean-NOx trap and Urea SCR for NOx control. Results of durability tests performed on SCR were presented in this presentation.

Hajime Ishii (NTSEL-Japan) presented results of comparison of ammonia continuous measurement techniques from an SCR vehicle. In this study, experiments were performed on urea SCR vehicle with constant and transient cycles and data from four types of continuous measurement methods (Dual SLC, Mass Spectrometry, FTIR, and

Diode Laser Spectrometry) is compared and evaluated. The Mass Spectrometer performed the best in terms on sensitivity, and the Diode Laser Spectrometer in terms on response.

Joe Patchett and Edgar Huennekes (Engelhard) presented the case for ammonia oxidation catalysts in SCR systems. Unreacted ammonia leaving SCR can contribute to particulate formation. Ammonia oxidation catalyst (AMOX) may be used to remove ammonia. Effectiveness of AMOX catalyst and some of the operating characteristics are evaluated using benchflow and heavy duty diesel engine. AMOX is found to be effective in removing ammonia without excessive NOx or N2O formation. The selectivity and activity of this catalyst is strongly dependent on the operating conditions. Transient operation is more beneficial than steady state. NH3 to NOx ratio highly effects performance of the catalyst.

John Storey (ORNL) gave presentation on urea decomposition and storage under light-duty diesel conditions (150-300C). Urea decomposition can lead to the formation of several undesirable species. Understanding low-temperature urea behavior is a key to developing effective and efficient SCR systems for light-duty vehicles. Urea decomposition on the catalyst surface causes higher selectivity to N2O in overoxidized conditions, and higher emissions on NCN during NH3 slip conditions. Controlling urea decomposition upstream of SCR and NO2/NO ratio may lead to very high NOx conversion per very small volume SCRs.

Cliff Kowall (Hi-Lite) summarized recent work on CFD modeling of urea-SCR dosing and spray systems. Topics covered included performance specifications, key design variables, and application design. Specific design issues included spray placement, spray distribution, droplet evaporation, and clogging and deposits. The CFD platform being used by Hi-Lite for these studies is the AVL FIRE Program. Cliff's overall conclusions for urea-SCR included:

- SCR remains the only proven technology for NOx reduction
- CFD modeling is cost effective way to study the system
- Key development needs are:
    - Better injection valves with improved mixing, less wall impingement, and fewer places for deposition
    - Operating strategies that minimize deposition by controlling exhaust gas and wall temperatures
    - More experimental validation data
    - Improved understanding of urea chemistry
    - Improved concepts for liquid storage on vehicle

Jonathon Male (GE) summarized recent work at GE on high throughput combinatorial chemistry and its application to the development of HC SCR catalysts. Initially, Jonathon discussed the types of catalyst design issues (e.g., catalyst composition, binders, fabrication methods, reductant mix, and operating strategy) that are most readily addressed with combinatorial methods. Next he discussed specific methods for setting up and implementing combinatorial studies, including parametric arrays, genetic algorithms, reactor design and control, data management, scalability, reliability, and statistical quality control. Jonathon concluded with example results for an alumina-supported silver HC-SCR catalyst. Even after promising candidate catalyst powders have been identified in the high throughput reactor, he pointed out that there are significant risks associated with transferring the catalyst to ceramic structured supports and their subsequent NOx reduction activity under realistic conditions of high flowrate, reduced volume, and extended operation in the presence of poisons such as sulfur. GE is continuing to work with PNNL to develop oxygenated reductants from diesel exhaust because these appear to be optimal for supported silver HC-SCR catalysts.

Dick Blint (GM) reviewed recent developments in the DOE-Industry CRADA activity on "Discovery of New NOx Reduction Catalysts for CIDI Engines Using Combinatorial Techniques" (DE-FC26-02NT41218). His discussion included a brief review of the history of this project, which was initiated in 2002 with a 65% cost share by DOE. The project focus is on SCR with reductants from the fuel (e.g.; n-octane, iso-octane). Engelhard is a key industrial partner and will likely supply any catalyst products developed under the program. So far, several thousand new catalyst materials have been evaluated under the program and approximately 10% have exhibited promising catalytic activity and are now undergoing further evaluation. One of the products of the project to date is an informatics software package for processing the output of high throughput combinatorial experiments.

Ed Jobson (Volvo) presented resent results of NOx reduction investigation performed on new catalyst materials based on Cu-ZSM5 technology and Ag-Alumina. Kinetic investigations and full scale tests have been performed. It was observed that NOx was reduced by HC and not H2 or CO on Cu-ZSM5 based catalyst. Also, NOx conversion's dependence on oxygen, water concentration and temperature has been investigated. The results confirm a continued progress in material development toward increased stability and improved hydrothermal stability.

Kalyana Chakravarthy (ORNL) presented a summary of observation on SCR kinetics based on the open literature. Zeolite catalysts (based mostly on meal-ion-exchanged ZSM-5) for SCR of lean NOx offer certain advantages over V2O5 catalysts (especially Fe-ZSM-5). Kalyana argued that while there are probably similar generic mechanisms are work in most zeolite urea-SCR catalysts, some degree of calibration will be needed for each catalyst sample. This need for calibration is the basis for developing a standard urea-SCR protocol analogous to the CLEERS LNT protocol. It is anticipated that results from this protocol can be used to develop global reaction kinetics that can be used for device simulation. Key remaining unknowns regarding urea-SCR modeling include:

- Urea to ammonia conversion on zeolites, especially below 250 °C
- The impact of spray hydrodynamics, heat & mass transfer, uniformity on reaction rates
- Possible formation of melamine
- The role of HNCO
- Competitive adsorption of NOx and NH3 on zeolites