

NOx Control and Measurement Technology for Heavy-Duty Diesel Engines

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Objectives

- Improve diesel engine-catalyst system efficiency through detailed characterization of chemistry and degradation mechanisms. This objective is based on bench-scale research.
- Work with industrial partner to develop full scale engine-catalyst systems to meet efficiency goals while complying with emissions regulations.

Approach

- Develop improved analytical techniques for characterizing combustion and catalyst chemistry.
- Evaluate reaction order and contribution, and deactivation-method effects based on bench-scale studies.
- Evaluate the effectiveness/efficiency of select engine-system parameters (e.g., operation strategies, fuel formulations and catalyst) to realize efficiency goals on full-scale engine-catalyst systems.

Accomplishments

- Developed minimally invasive analytical technique for in-situ intra-catalyst measurement of transient temperature distributions.
- Improved H2-SpaciMS to provide better temporal response for measurement of polar species concentrations.
- Evaluated timing, priority and significance of various detailed reactions involved in reactor chemistry relevant to the CRADA objectives.
- Quantified select effects of deactivation mechanisms on the efficiency of reactors relevant to the CRADA objectives.
- Quantified engine-out species pools associated with engine-managed reductant-generation strategies at various engine conditions.
- Supported CRADA objectives through two separate campaigns involving field application of the H2-SpaciMS and PhosphorT instruments at the industrial partner's research facilities.

Future Directions

- Quantify select effects of additional deactivation mechanisms on the efficiency of reactors relevant to the CRADA objectives.
- Additional reforming reactions will be studied. As with the FY04 work on different reactions, this work will evaluate the timing, priority and significance of various detailed reactions involved in reactor chemistry relevant to the CRADA objectives.
- Investigate variations in reaction effectiveness with reaction parameters. The purpose of this task is correlate reaction efficiency with fuel penalty, and to better define an optimum strategy.
- Full engine-systems research, will characterize the engine-, and catalyst(s)-out species pools resulting from engine-managed operation with different low-sulfur fuels. This will help guide fuel selection for follow-on work. The primary research goal for FY2005 is to identify pathways for improved fuel economy

Introduction

Increasing expectations for efficiency, fuel economy, and clean emissions from heavy-duty vehicles requires corresponding improvements in system design. The realm of expectation is now sufficiently high to require carefully integrated engine-catalyst-control systems working in precise concert. This level of design and control requires detailed knowledge of the combustion and catalyst chemistry; i.e., what reactants makes the catalyst most efficient, what is the order and significance of reactions throughout the system, and how can the engine/system be controlled to enhance catalyst efficiency? This CRADA takes a parallel approach with highly controlled bench-scale and more final-product-indicative full-engine-scale research to address these issues.

Approach

The big-picture approach that has been used in this CRADA is to combine the unique resources available at Cummins Inc. and Oak Ridge National Laboratory to improve the efficiency of the target diesel-engine systems. The approach uses parallel bench-component- and full-engine-scale investigations. The goal of such studies is to establish a more detailed understanding of the component and system operation, so that pathways to efficiency improvements and technology barriers can be identified. These technology limitations include analytical technique deficiencies that limit the detail with which the system can be characterized. As suggested by the project title, developing advanced measurement technology when necessary to improve characterization ability is also a central purpose of this project. Continual refinement of detailed system knowledge and the analytical techniques used to establish that knowledge enhances the team's ability to correspondingly improve the efficiency, fuel economy and emissions of the diesel-engine system.

Results

Development of advanced measurement technologies continues to be an area of success for this CRADA. This success builds on that of the spatially resolved capillary inlet mass spectrometer, or SpaciMS, which allows for minimally invasive intra-catalyst measurement of transient species distributions. Later versions of this instrument, the H₂-SpaciMS, allowed for quantifying of hydrogen concentration which is a very active and important species in catalyst function. Further improvements to the H₂-SpaciMS in FY2004 provided improved temporal resolution for measurement of polar compounds. The SpaciMS allows measurement of a broad range of species, and hence detailed characterization of the evolution of the various chemical reactions ongoing within the catalyst reactor. In addition to species, transient temperature distributions are critical to understanding catalyst chemistry. In FY2004 a new instrument, PhosphorT, for

providing the requisite temperature measurements was developed and field demonstrated. The PhosphorT instrument is based on phosphor thermography and uses optical fiber physical probes to provide intra-reactor minimally invasive temperature measurements. Both the H2-SpaciMS and PhosphorT instruments were applied along with conventional analytical techniques at the Cummins Technical Center in FY2004 to study detailed chemistry relevant to the CRADA objectives. This work allowed the priority of the various reactions to be ranked. More specifically, via the intra-catalyst measurements, we have quantified the phase of the various reactions; the reaction phase is consistent with step-wise completion of the various reactions in the order of their priority. This detailed understanding is relevant to optimizing the efficiency of systems defined in the CRADA objective.

The Phosphor Thermography instrument was developed to quantify transient temperature distributions throughout an operating catalyst. Figure 1a shows a schematic of the instrument, and Fig.1b shows a photograph of a fieldable version of the instrument. The instrument is based on the temperature-dependant phosphorescence lifetime of rare-earth-doped ceramic phosphors. A 337-nm laser is injected into one (pump) leg of a fiber coupler to excite a phosphor deposited on the tip of a gold-coated fiber. The gold coating allows for high-temperature applications up to 750C. The phosphor is laser promoted to long-lived excited states which decay via phosphorescence in the 650-nm range. Some of the phosphorescence is captured by the same optical fiber used to deliver the pump light, and is directed to a second (detection) leg of the fiber coupler. The light emitted from the detection leg is filtered to reject pump light, and detected via a photomultiplier tube. The phosphorescence signal displays an exponential decay with a time constant, τ , proportional to temperature. The PMT signal is monitored at 400kHz and analyzed via a LabView program to actively determine the phosphorescence time constant. The time constant can be measured and converted to temperature at rates up to ca. 2Hz. Temperature gradients are resolved by translating the fiber's phosphor tip.

Figure 2 shows the PhosphorT instrument (black box on the cart) being used for bench-scale catalyst measurements at a Cummins Technical Center laboratory. Post Doc Shawn Goedeke is leaning on a tube furnace containing the catalyst core sample, and inserting the phosphor-tipped optical fiber into the reactor outlet. The silver box behind the tube furnace in Fig.2 is the H2-SpaciMS which sampled at five positions throughout the reactor via capillaries inserted in the reactor inlet. Some of the conventional analyzers used for additional analysis can be seen in Fig.2. Figure 3 shows intra-catalyst transient temperature distributions measured via the PhosphorT instrument. Temperature dynamics are shown for seven positions within the reactor and indicated by ju , where j is a unit multiple; $0u$ is the catalyst inlet face, $-1u$ is one unit before the inlet face, and positive j values are corresponding unit multiples into the catalyst. The temperature values for the various curves are absolute; i.e., the curves are not offset. Sharp or high-frequency temperature transients are indicative of exothermic reactions, and lower-frequency temperature transients are indicative of bulk heat transfer. It is apparent from the Fig.3 that the $0u$ position is actually just inside the catalyst, rather than at the catalyst face; or that exothermic reactions occur at the catalyst face. The detailed nature of the thermal wave's progression through the catalyst is characterized by the data of Fig.3 for certain catalyst conditions and reactants. These results show that at many positions within the catalyst the peak temperature occurs at times significantly removed from the initial exotherm; i.e., the time of the leading exotherm edge at the $0u$ position. Such delayed heating is inefficient to some catalyst processes, and suggests that alternate parameters might provide improved efficiency. Figure 3 indicates that exothermic reactions occur at positions $0u$ through $4u$ at early times. By correlating the PhosphorT measurements with corresponding H2-SpaciMS measurements, more detail of the catalyst chemistry is revealed. For instance, the exotherms apparent in Fig.3 at positions $1u$ through $4u$ are attributable to a different reaction than causes the exotherm at the $0u$ position.

I.e., exothermic reaction A occurs very fast and at the very front of the catalyst. Once reaction A is complete, a second exothermic reaction B occurs. This type of detail is being used by the CRADA team to improve the efficiency and fuel economy of diesel catalyst systems.

In the Engine Systems section of the CRADA, a full engine system was used to assess the reductant pool resulting from engine-managed reductant generation when using DECSE and Chevron Phillips 2007 Ultra-Low-Sulfur fuels. The CP 2007 ULSD fuel is what Chevron Phillips anticipates providing at the pump in 2007. The species pool was characterized using a range of analytical techniques available at ORNL FEERC to measure several species including CH₄, Total (non-CH₄) HC, detailed HC speciation via GC/MS, NO, NO₂, O₂, CO, CO₂, H₂ (via H₂-SpaciMS) and smoke number. The engine performance, emissions and reductant pool generation were found to be similar for DECSE and the CP 2007 ULSD fuels. Based on these results, an overview of the basic fuel compositions was performed for a range of fuels being studied at ORNL FEERC including, Pump, BP-15, ECD1, Certification, CP 2007 ULSD, 10% Aromatic and DECSE. Figure 4 a, b and c show the base fuel chromatogram for ECD1, CP 2007 ULSD and DECSE fuels, respectively. The distinct features in Fig. 4 are straight-chain saturated compounds, alkanes, while the broad envelop is composed of a soup of other compounds including branched alkanes, alkenes, aromatics... It is apparent from Fig.4 that ECD1 has a much broader range of straight-chain alkanes compared to both CP ULSD and DECSE fuels. The CP fuels have a bimodal HC envelope; the high molecular weight alkanes and alkenes that make up one lobe of the HC envelop are apparent in the combustion exhaust. The aromatic content of the CP fuels is apparently comprised of a fewer number of aromatics, which are primarily confined to lower molecular weight compounds. These are some of the distinct differences in the CP fuels (Certification, CP ULSD, 10% Aromatic and DECSE) and both the BP (BP-15, ECD1) and pump fuels; both BP fuels are similar in terms of base-fuel chromatogram to current pump diesel. There are dramatic differences in the slated 2007 fuel intended by BP (ECD1) and CP (ULSD). Ongoing and future work will further characterize the fuel differences, specifically in terms of aromatic content. The fuels-effects research is co-supported by the the Fuels Technology activity in the Office of FreedomCAR and Vehicle Technology. In light of the similarities in the DECSE and CP ULSD fuels, the similarities in the engine-managed performance resulting from these fuels may not be unexpected. FY2005 work will investigate engine-managed performance with a very different fuel such as ECD1 to highlight fuel effects.

Conclusions

A new analytical technique for quantifying transient temperature distributions within operating reactors was developed and demonstrated. This diagnostic was used in parallel with the H₂-SpaciMS to quantify detailed intra-catalyst species and temperature dynamics in experiments at both the Cummins Technical Center and ORNL FEERC. That work has established a new understanding of reaction order, priority and distribution within the catalyst, and is allowing engine/catalyst system improvements as defined in the CRADA objectives. Full-scale engine-system experiments compared the engine-out reductant pool associated with engine-managed reductant generation for two fuels. We have found that the composition of the 2007 diesel fuels proposed by BP and Chevron Phillips are dramatically different, and expect corresponding differences in the combustion product species pools. Follow-on experiments will detail the species pools for the two 2007 fuels associated with engine-managed reductant generation throughout the engine-catalyst system.

FY 2004 Publications/Presentations

1. Jae-Soon Choi, Trevor Miller, William S. Epling, Shean P. Huff, Kalyana Chakravarthy, Katey E. Lenox, William P. Partridge, C. Stuart Daw, "Regeneration behavior of NO_x storage-

reduction catalysts under simulated or realistic diesel exhaust," poster presentation at the 4th Department of Energy National Laboratory Catalysis Conference, Oak Ridge, Tennessee, October 2003.

Acronyms

BP:	British Petroleum
CP :	Chevron Phillips
CRADA:	Cooperative Research And Development Agreement
DECSE:	Diesel Emissions Control Sulfur Effects
FEERC:	Fuels Engines and Emissions Research Center
FY#:	Fiscal Year #
H2-SpaciMS:	Hydrogen-SpaciMS
ORNL:	Oak Ridge National Laboratory
PhosphorT:	Phosphor Thermography
PMT:	Photomultiplier Tube
SpaciMS:	Spatially Resolved Capillary Inlet Mass Spectrometer
ULSD:	Ultra-Low Sulfur Diesel

Figure Captions

Figure 1. Schematic (a) and photograph (b) of the Phosphor Thermography instrument.

Figure 2. Bench-reactor experiments to measurement of in-situ intra-catalyst transient temperature and species distributions via PhosphorT and H2-SpaciMS.

Figure 3. Intra-catalyst transient temperature distributions associated with dynamic catalyst operation.

Figure 4. Base fuel chromatogram for ECD1 (a), Chevron Phillips 2007 ULSD (b) and DECSE (c).