II.D.1 Health Effects from Advanced Combustion and Fuel Technologies

John Storey (Primary Contact), Teresa Barone, Jim Parks, Sam Lewis, Maggie Connatser
Oak Ridge National Laboratory (ORNL)
P.O. Box 2008, MS 6472
Oak Ridge, TN 37831-6472

DOE Technology Development Manager:
James J. Eberhardt

Objectives

- Understand potential impact of developing fuel, combustion, and aftertreatment technologies on air quality and, thereby, human health.
- Quantify mobile source air toxic emissions from advanced technologies.
- Link emissions measured in laboratory setting to air quality impact, and thereby, health impact.

Accomplishments

- Completed measurements of mobile source air toxics (MSATs) from light-duty vehicles operating on intermediate blends of ethanol (E10, E15 and E20):
  - Higher ethanol blends decrease emissions of benzene, toluene, ethylbenzene, and xylenes (BTEX) over a driving cycle.
  - BTEX reduction proportionally higher than what would be expected from simple mixtures with ethanol which does not contain BTEX.
- Completed an intensive campaign to measure the morphology and effective density of diesel particulate matter (PM) from conventional and premixed charge compression ignition (PCCI) operation:
  - The difference in effective density of conventional diesel and PCCI PM depended on particle diameter.
  - Transmission electron microscopy (TEM) analysis of diesel particle morphology was conducted and compared to the particles generated using high-efficiency clean combustion (HECC) modes.
- Characterized particle size and number concentration emissions from a homogeneous charge compression ignition (HCCI) engine operating on surrogate gasoline fuels:
  - Combustion phasing for reduced fuel consumption and particle number concentration emissions was affected by fuel chemical composition.

Future Directions

- Characterize particulate emissions from a direct-injection spark ignition vehicle operating on gasoline and intermediate blends of ethanol.
- Examine mixed mode diesel particulate filter/lean-NOx trap/selectic catalytic reduction catalytic effects on MSATs.
- Reconcile idealized aggregate theory with PM samples collected under conventional and HECC conditions.

✧ ✧ ✧ ✧ ✧

Introduction

Scientists and engineers at national laboratories, universities, and industrial companies are developing new fuels and energy efficient technologies for transportation, and the U.S. DOE is actively involved in this innovative research. However, care must be taken to insure that any new fuel or technology developed for transportation must not adversely directly impact human health or impact the health of the environment, which subsequently may impact human health. To address this need, DOE sponsors research studies on the potential health impacts of advanced technologies for transportation including advanced fuels, combustion techniques, and emissions controls (also known as "aftertreatment" or, more commonly, "catalytic converters"). DOE sponsored health impact research activities at ORNL are presented in this report.

ORNL conducts research on advanced fuel, combustion and emissions control technologies at the Fuels, Engines, and Emissions Research Center. As the research is being conducted on engine and chassis dynamometers, specific studies of the potential health impacts of the technologies are conducted by the ORNL team for DOE's health impacts activity. Results from ongoing ORNL studies in Fiscal Year 2009 are presented here. A major focus has been the impact of ethanol blends on emerging gasoline vehicle technologies. A second focus has been on the impact of advanced combustion regimes on the emissions of PM and MSATs. In the first study reported here, several in-use vehicles operating on intermediate ethanol blends were analyzed for emissions of gaseous MSATs. In the second study, PM emissions from two engines operating in the advanced diesel combustion modes of HCCI and PCCI were characterized.

Approach

Gaseous MSATs from Vehicles Fueled with Intermediate Blends of Ethanol

A series of in-use light-duty vehicles (model years from 1999–2007) were acquired by ORNL and evaluated as part of a larger study on the use of intermediate blends of ethanol in the existing fleet [1]. The vehicles were driven over the LA92, also known as the Unified Cycle, a driving cycle that is commonly used for emissions inventory and other in-use studies. The LA92 is considered to be more representative of in-use driving than the Federal Test Procedure (FTP). In addition to standard emissions, gaseous MSAT emissions were collected in canisters and analyzed with gas chromatography/mass spectrometry.

PM Characteristics for PCCI Diesel Engines

A Mercedes 1.7-liter 4-cylinder diesel engine was operated at 1,500 rpm, and 2.6 brake mean effective pressure (BMEP), a point representative of light-duty vehicle cruise operation, on an engine dynamometer. The engine operated in both production calibration conditions and under PCCI combustion conditions. The engine was not equipped with any aftertreatment. Utilizing a special aerosol mass analyzer (Kanomax APM-3600) in combination with a differential mobility analyzer (DMA; TSI 3081), the effective density of the PM in both conventional and PCCI modes was measured. At the same time, size selected PM was collected for morphological studies and analyzed by TEM.

PM and MSATs from an HCCI Engine Operating on Surrogate Gasoline Fuels

The effect of fuel chemical composition on engine efficiency and emissions was investigated. A single-cylinder research engine for which performance is dominated by fuel effects was used. Because the chemical composition of gasoline is highly complex, the engine was operated with three surrogate gasoline fuels with representative functional groups, branched alkane, straight chain alkane, aromatic, and alcohol. The fuels had the following compositions: 87% iso-octane and 13% n-heptane (iso-octane reference fuel); 58% iso-octane, 9% n-heptane and 33% ethanol (iso-octane reference fuel with ethanol); and 73% toluene and 27% n-heptane (toluene reference fuel). Thermal efficiency and fuel consumption were investigated by combustion phasing experiments in which the intake air and fuel mixture temperature was decreased such that the combustion event was delayed. PM number concentration and diameter were measured with a nano-scanning mobility particle sizer (TSI 3085 DMA, TSI 3025 condensation particle counter) following dilution in a microtunnel. The dilution ratio was factored into the calculation for the emissions. Fuel consumption and PM emissions were compared for varying crank angle degree at which 50% of the fuel mass fraction burned.

Results

Gaseous MSATs from Vehicles Fueled with Intermediate Blends of Ethanol

Example gaseous MSAT emissions with intermediate blends of ethanol are shown for two different vehicles in Figure 1. The only measurable emissions essentially occurred in Bag 1 of the driving cycle. The presence of ethanol definitely lowers the emissions of BTEX by amounts beyond the simple substitution percentages. This result is consistent with previous work on an E85 vehicle showing dramatic reductions in BTEX [2].

PM Characteristics for PCCI Diesel Engines

Previous studies have indicated that unburned hydrocarbon (HC) emissions are higher for PCCI than conventional combustion [3,4]. Some HC species in the gas phase may condense on soot present in the exhaust or nucleate to form semi-volatile PM. Soot coated with condensed liquid HCs may act as a vehicle for transporting biologically active HC compounds into the lung. Furthermore, if the soot is immersed in liquid hydrocarbons, the soot effective density will be greater than if the soot were dry. Thus, we expected to find

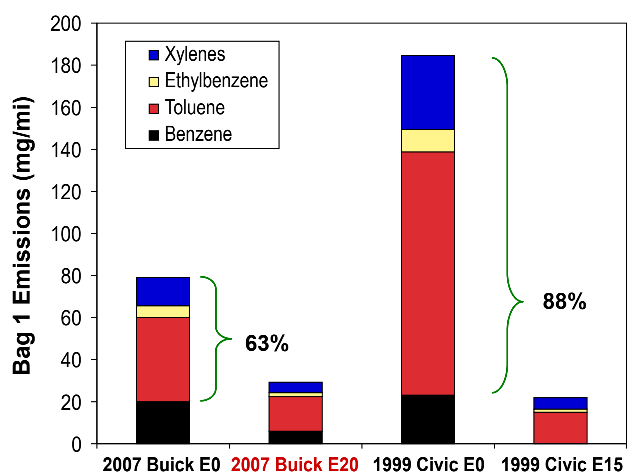

FIGURE 1. Intermediate ethanol blends substantially lower MSATs such as benzene, toluene, ethylbenzene and xylenes. Note that these are calculated for Bag 1 only of the FTP cycle since virtually no emissions of these compounds are detected in Bags 2 and 3.

higher effective densities for PCCI soot. However, our results show that the effective density of PCCI PM was similar to conventional diesel PM for 50 and 100 nm particles and less than conventional diesel PM for 150 nm particles (Figure 2). In addition, a liquid HC layer was not present on PCCI soot as indicated by TEM analysis (Figure 3). However, it is possible that the liquid hydrocarbons may be present in the pores of the soot primary particles [5]. Idealized aggregate theory predicts that PCCI PM may have a lower effective density than conventional diesel PM if the primary particle diameters are smaller. To test this hypothesis, the diameter of approximately 13,000 primary particles was measured using the image analysis technique of Xiong and Friedlander [6]. The average primary particle diameter of PCCI soot (21 ± 3 nm) was less than that for conventional diesel soot (25 ± 4) for 150 nm particles, consistent with Idealized Aggregate Theory. A report of these results is being prepared for publication.

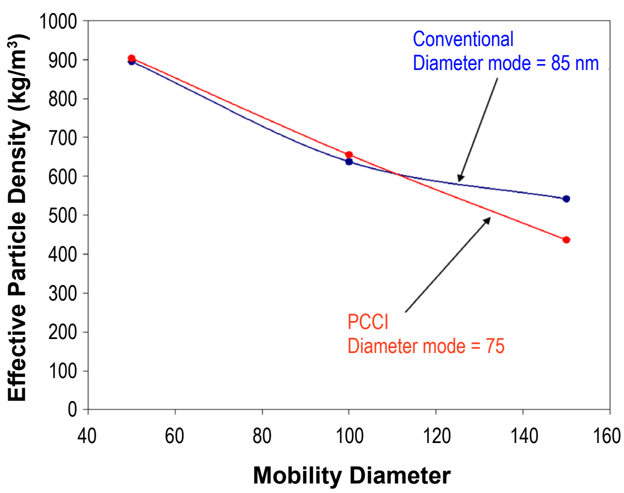

FIGURE 2. Comparison of PCCI (red) and conventional (blue) particle effective densities for 50, 100, and 150 nm electrical mobility diameters. (Engine conditions: 1,500 rpm, 2.6 BMEP)

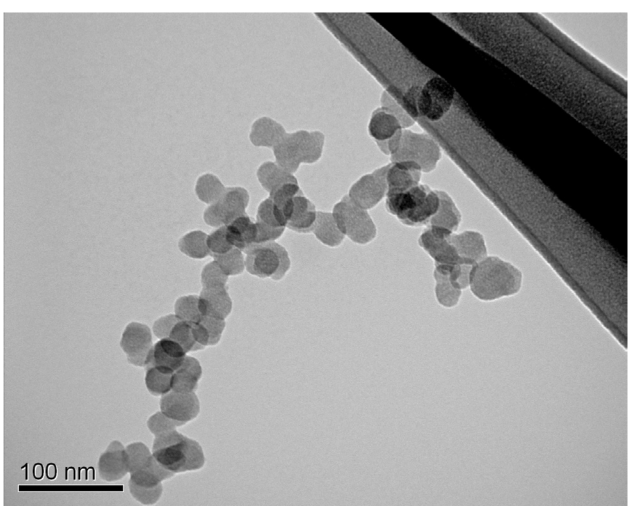

FIGURE 3. TEM image of PCCI soot with 100 nm electrical mobility diameter. (Engine conditions: 1,500 rpm, 2.6 BMEP)

PM and MSATs from an HCCI Engine Operating on Surrogate Gasoline Fuels

The effect of fuel chemical composition on HCCI engine efficiency and emissions was compared for the iso-octane reference fuel, iso-octane reference fuel with ethanol, and toluene reference fuel. The results indicated that combustion phasing for minimum fuel consumption differs depending on the fuel chemical composition. The lowest fuel consumption was achieved with the iso-octane reference fuel. Because the energy content of ethanol is lower than the other fuels, a comparison was made in terms of thermal efficiency, and the iso-octane reference fuel was again the most efficient. At the crank angle degree for 50% mass fraction burned and the minimum in fuel consumption for each fuel, the iso-octane reference fuel had the lowest PM number concentration emissions ($1.0 \pm 0.4 \times 10^5$ part./cm^3). Delaying the combustion event of the ethanol and toluene fuels, resulted in significant reduction of PM number concentration and only a slight rise in fuel consumption, such that the emissions were close to that for the iso-octane reference fuel. The fuel consumption and PM number concentration emissions results are shown in Figure 4 for the iso-octane reference fuel. For all fuels and conditions, the particle geometric mean diameter ranged from 10 to 30 nm. At the minimum fuel consumption point, the iso-octane reference fuel PM emissions had geometric mean diameter of 14 ± 1 nm. These findings

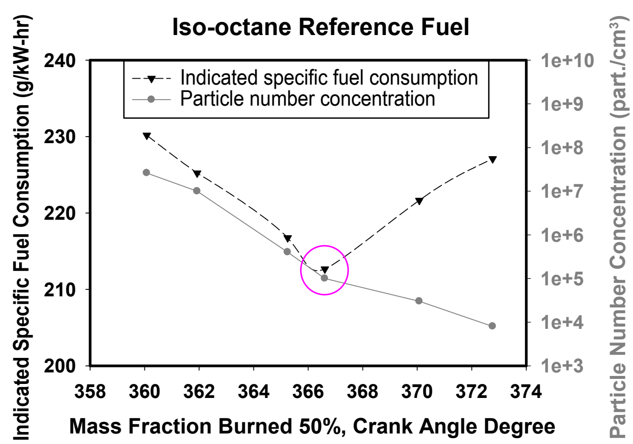

FIGURE 4. HCCI engine cycle timing for minimum fuel consumption (black) and particle number concentration emissions for each operating point (grey). The operating point for simultaneous low emissions and fuel consumption is circled (pink). (Engine conditions: 1,800 rpm, nominal 3.0 indicated mean effective pressure)

may be of use in future models of fuel effects on engine efficiency and emissions.

Conclusions

- Intermediate Blends:
  - Benzene, toluene, ethylbenzene and xylenes decrease with increasing ethanol content.
- PCCI and Conventional Diesel PM Effective Density:
  - The effective density of 50 and 100 nm PCCI PM was nearly the same as conventional diesel PM. For 150 nm particles, PCCI PM effective density was lower than conventional diesel PM.
  - The lower effective density of 150 nm PCCI PM may be the result of smaller soot primary particle diameters; based on TEM and image analysis, the average primary particle diameter of PCCI soot was 21 ± 3 nm and of conventional diesel soot 25 ± 4 nm.
- HCCI Gasoline Surrogate Fuels:
  - The lowest PM number concentration emissions and highest thermal efficiency occurred for the iso-octane reference fuel.
  - For the ethanol and toluene fuels, delaying the combustion event past the point of minimum fuel consumption reduced PM number concentration emissions substantially while only increasing fuel consumption slightly.
  - The PM geometric mean diameter for all fuels and combustion phasing conditions ranged from 10 to 30 nm.

References

1. Knoll, Keith, Brian West, Wendy Clark, Ronald Graves, John Orban, Steve Przesmizki, Timothy Theiss, "Effects of Intermediate Ethanol Blends on Legacy Vehicles and Msall Non-Road engines, Report 1 – Updated," ORNL/TM-2008-117, February 2009.

2. West, B., Lopez, A., Theiss, T., Graves, R., Storey, J., Lewis, S., "Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 Biopower", SAE Paper Number 2007-01-3994. Society of Automotive Engineers, Warrendale. 2007.

3. Sluder, C.S., Wagner, R.M., Lewis, S.A., Storey, J.M., "Fuel Property Effects on Emissions From High Efficiency Clean Combustion in a Diesel Engine," SAE Paper Number 2006-01-0080. Society of Automotive Engineers, Warrendale, 2006.

4. Storey, J.M.E., Lewis, S.A. Sr., Parks, J.E. II, Szybist, J.P., Barone, T.L., Prikhodko, V.Y., "Mobile Source Air Toxics (MSATs) from High Efficiency Clean Combustion in Diesel Engines", *SAE Int. J. Engines*, Vol. 1, pp. 1157-1166, 2008.

5. Ishiguro, T., Suzuki, N., Fujitani, Y. and Morimoto, H. (1991) Microstructural changes of diesel soot during oxidation. Combustion and Flame, 85, 1-6.

6. Xiong, C. and Friedlander, S.K. "Morphological properties of atmospheric aerosol aggregates." Proc. Natl. Acad. Sci., 98, 11851-11856. 2001.

FY 2009 Publications/Presentations

1. John Storey, James Parks II, Sam Lewis, Laura Kranendonk, and Teresa Barone, "Measurement and Characterization of Unregulated Emissions from Advanced Technologies," *Presentation at the DOE Vehicle Technologies Merit Review* on May 21, 2009.

2. Teresa Barone, Anshuman Lall, John Storey, Michael Zachariah, Vitaly Prikhodko, James Parks, "A Comparison of Advanced and Conventional Diesel Combustion Particulate Matter Emissions: Particle Effective Density," In preparation.

3. Teresa Barone, John Storey, Scott Eaton, Bruce Bunting, Raynella Connatser, and Samuel Lewis, "The Influence of Fuel Chemical Composition on Particle Emissions from an Advanced Combustion Engine," *Poster Presentation at the* American Association of Aerosol Research 28th Annual Conference. Minneapolis, MN. October 2009.

4. Teresa Barone, John Storey, and Norberto Domingo, "Durability Analysis of a Field-Aged Diesel Particulate Filter Used in a School Bus Retrofit Program" *Oral Presentation* at the American Institute of Chemical Engineers Annual Meeting in Nashville, TN in November, 2009.