Investigation on Dioxins Formation by Heavy-Duty Diesel Engines with Selective Catalytic Reduction (SCR) Technology

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Introduction

- Selective Catalytic Reduction (SCR) Technology was one of the key technologies used to help truck engine manufacturers meet the stringent 2010 NO_x emission standard of 0.2 g/hp-hr on heavy-duty diesel engines (HDDE). SCR converts residual NO_x (NO and NO_2) into nitrogen and water vapor in the presence of a reducing agent (such as ammonia) and a metal catalyst. The most effective catalyst used in SCR technology contains copper in the form of copper-zeolite (CuZ). It had been shown in earlier studies that dioxins were formed in the presence of chlorine (or chlorine-containing compounds) and metals (including copper) at elevated temperatures (see Figure 1). Whether or not dioxins would be formed by the HDDE with the SCR technology remained unknown.

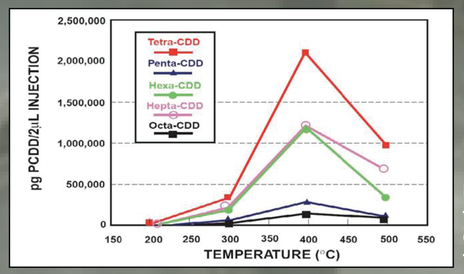

Figure 1. Formation of Dioxins from Chlorophenol with a Cu(II) Catalyst as a Function of Temperature (Gullet *et al*., 1977)

Background

- Dioxins are made up of two families of three-ring chemical compounds: polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (Figure 2). Dioxins are unintentional by products of chemical processes and incomplete combustions of chlorine-containing materials. Some of the PCDDs and PCDFs, such as 2,3,7,8-TCDD and 2,3,7,8-TCDF (Figure 3), have been shown to be potent carcinogens to certain mammals. These chemical agents also weaken immune responses in the offspring of animals exposed to them during pregnancy. Due to extremely high acute toxicities in selected lab animals and their potential chronic toxicities to humans, dioxins need to be monitored at very low concentrations. The only reliable analytical technique for ultra low level dioxins detection is by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS, Figure 4).

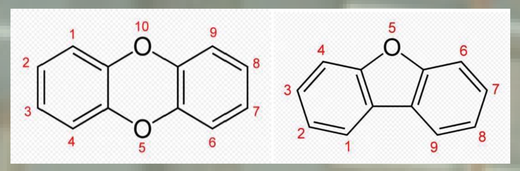

Figure 2. Basic Structures of PCDDs (left) and PCDFs

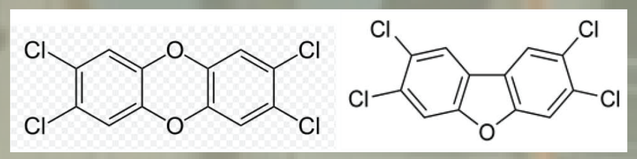

Figure 3. 2,3,7,8-TCDD (left) and 2,3,7,8-TCDF

Objectives

- Determine potential sources for dioxins production in a HD diesel engine emission test cell
- Investigate dioxin formation on HDDE both with and without CuZ SCR technology
- Measure the effects of chlorine levels in fuels on dioxins formation
- Discover the optimal engine operating temperature for dioxins formation

Figure 4. HRGC/HRMS

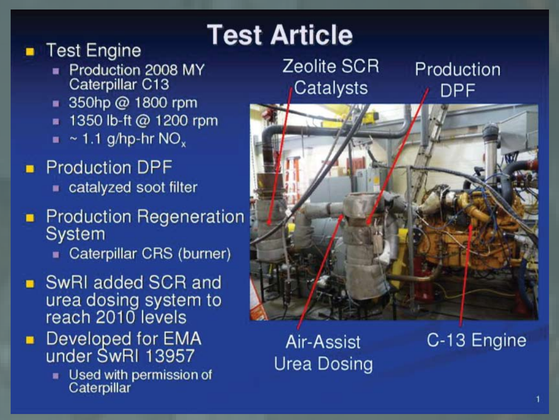

Figure 5. Test Engine: Catapillar 2008 Production Engine C13 with SCR

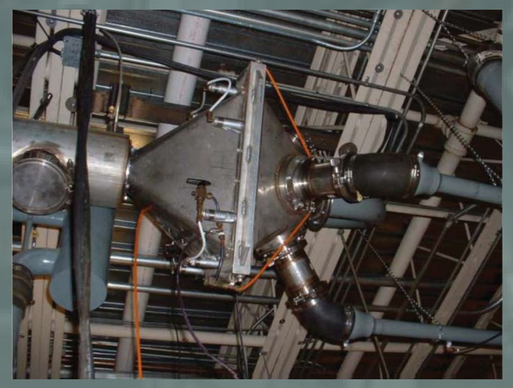

Figure 6. Sampling Manifold for the Filters and PUF/XAD-2/PUF Traps

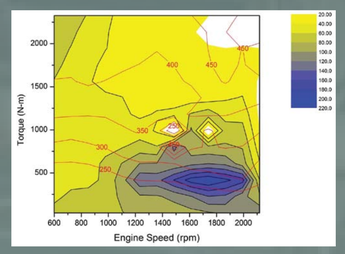

Figure 7. Caterpillar 2008 C13 DPF-Out Temperature Map, in degrees C

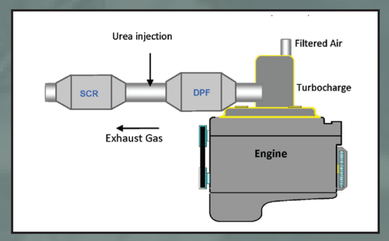

Figure 8. Engine with SCR and DPF Schematic Diagram

Technical Approaches

- Chlorine contents were measured in the fuel, lubricant, water and engine intake air.
- Emission testing was performed on production 2008 Caterpillar C13 engine modified to meet 2010 emission standards (Figure 5).
- Gaseous dioxins were collected on four-inch SS PUF/XAD-2 traps, and particulate matters were collected on glass fiber filters (Figure 6).
- Dioxins formation was investigated in HDDE under steady-state (SS) conditions with DPF only and with DPF-SCR system at temperatures between 250°C and 450°C with 50°C increments (Figure 7).
- Engines were tested with various configurations of CuZ SCR aftertreatment technologies under SS conditions with chlorine-doped fuel (Figure 8).
- An HD engine was tested under transient conditions both with and without aftertreatment (Figure 9).
- Three aftertreatment technologies were tested (DOC-SCR, SCR only, and SCR-AMOX) under SS operation at 300°C and 400°C with chlorine-doped fuel (820 parts per billions by weight). Four conditions were tested: a) Engine-out, b) DOC-SCR, c) SCR only and d) SCR-AMOX.

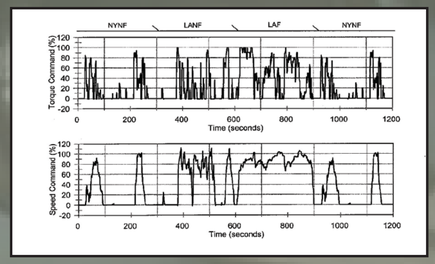

Figure 9. Graphic Representation of Torque and Speed Commands for the EPA Transient Cycle for Heavy-Duty Engines

Results

- The cooling tower water had 17 parts per million (ppm) chlorine.
- Chlorine in new and used lube was 144 and 174 ppm, respectively.
- Trace levels of chlorinated organic compounds were found in engine intake air.
- Metals found in the new lube for Al, Cu, Fe, Ni and Zn were 5.5, 0.19, 12, 1.1 and 1180 ppm, respectively
- Metals found in the used lube for Al, Cu, Fe, Ni and Zn were 87, 394, 166, 22 and 920 ppm, respectively.
- Dioxins were found in tunnel blanks with the levels not correlated with tunnel temperatures.
- No increase in dioxins formation was observed over the 250 to 450°C range under SS conditions, and the dioxin levels with the DPF-SCR system were similar to the levels of DPF only.
- Under the transient engine conditions, the DPF-out dioxin levels were similar to levels from the DPF-SCR system.

Conclusions

- While increases in dioxin formation were suspected with Cu-based catalysts based on previous work, no increases in dioxin formation were observed in this study. The three SCR technologies investigated in this project showed no significant increase in dioxin formation even when the fuel was doped to ten times the normal chlorine concentration. In addition, dioxin formation was not dependent on the exhaust temperature or transient operation.

Acknowledgment

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