



A New Method for Quantifying Urea and Urea Thermal Decomposition By-products

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Introduction

Most heavy-duty engine manufacturers choose selective catalytic reduction (SCR) technology as an essential part of their exhaust aftertreatment system. SCR uses a liquid reductant injected upstream of a catalytic converter to reduce NO_x emissions. The reductant, diesel exhaust fluid (DEF), is composed of 32.5% urea in water.

The urea thermal decomposition reaction includes the formation of ammonia and isocyanic acid as intermediate products. Isocyanic acid can initiate the formation of larger molecular weight compounds such as cyanuric acid and dicyandimide. These compounds are responsible for the formation of deposits on the walls of the decomposition reactor walls, which could increase overall particulate matter (PM) emissions.

Objectives

The objectives of this project were to validate a new analytical method to identify and quantify urea and six major by-products of urea thermal decomposition, and to apply this method for both deposit samples and PM collected on sample filters.

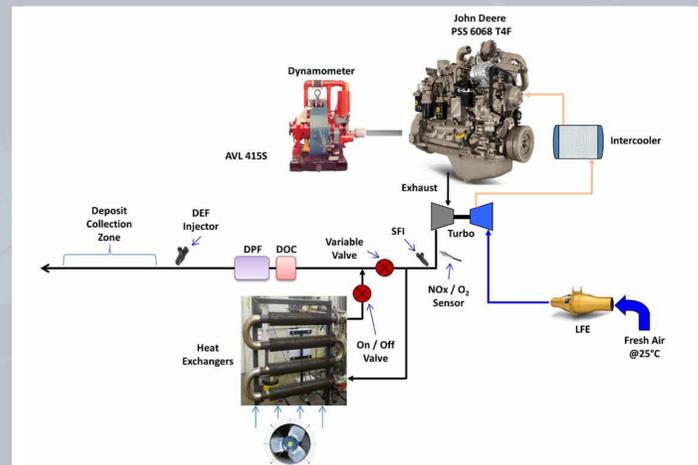
Technical Approach

Task 1. Urea Deposit Generation

The goal of this task was to generate urea-derived deposits in the DEF decomposition tube under various exhaust conditions with constant rate DEF injection. The urea deposit cycle was run under steady-state engine conditions. The diesel particulate filter (DPF) outlet temperature was maintained at a specified value ranging from 190°C to 340°C.

Task 2. PM Filters Generation Test Procedure

The goal of this task was to increase total PM mass on the filter to ensure that urea-related compounds exceeded the detection



Test cell schematic



limits. Two types of 47-mm filters were used for PM collection with an off-road diesel engine. Collection points were upstream (control) and downstream of the aftertreatment system.

Three sets of engine tests were performed on separate days. For Set 1 and Set 3, PM for each test cycle was collected on an individual filter. For Set 2, PM for five non-road transient cycles was collected on the same filter. For the ramped modal cycle, PM for four cycles was collected on the same filter.

Task 3. Analytical Test Procedures

Development

Both basic (pH 11.2) and acidic (pH 3.1) solvents were used for two-step extraction of acidic and basic compounds. Isotope labeled urea, cyanuric acid (CYA), and melamine (~250 ng) were added to the samples prior to extraction to monitor the analytical performance.

For the solid deposit samples with higher levels of compounds, one-step extraction was sufficient. Due to the extremely variable concentration of the compounds (from 95% to 5 ppm), multistep dilutions were used prior to the analyses.

Results and Discussion

Urea and Urea Decomposition Compounds Analytical Method Performance

Analytical performance and reliability of the method were evaluated by determining its precision, linearity, limit of detection (LOD), limit of quantification (LOQ) and accuracy. Both intra-day and inter-day precision of peak area for the standards with known concentrations were between 1% and 6% of the relative standard deviations for all compounds quantifying in positive mode and 13% for CYA quantifying in negative mode.

PM Composition Results

Three compounds including urea, CYA, and ammelide were detected in all of the PM samples collected downstream of the SCR during the second set of samples, while only two compounds were observed on PM collected

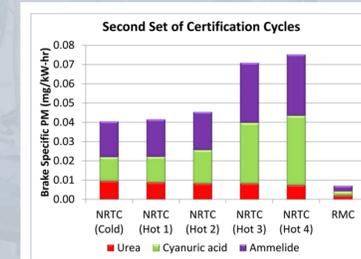
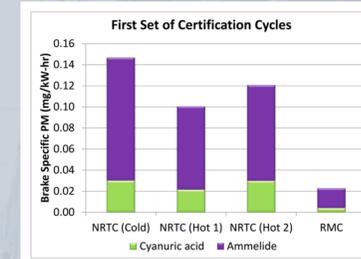
during the first set. The most abundant urea decomposition products were CYA and ammelide.

Three interesting phenomena were observed: a surprisingly high amount of CYA, a decrease of ammelide collected for the second set of PM filters, and a change in composition when PM was collected from several cycles on the same filter.

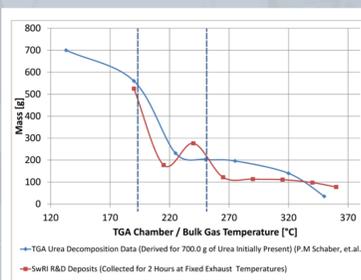
Solid Urea Derived Deposits Results

Urea deposits were generated in the DEF tube of the engine using the urea deposit test cycle. Following each two-hour test period, deposits were removed from the exhaust system to be weighed and analyzed for composition.

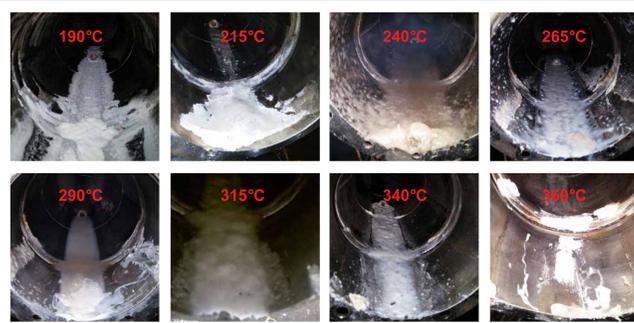
Following the start of injection, there was a sudden decrease in surface temperature due to wall film development and evaporation of the DEF. A gradual increase in surface temperature was noted due to the growth of a solid deposit, creating an insulating layer between the liquid



Urea-related compounds in particulate matter collected on PM filters during certification cycles

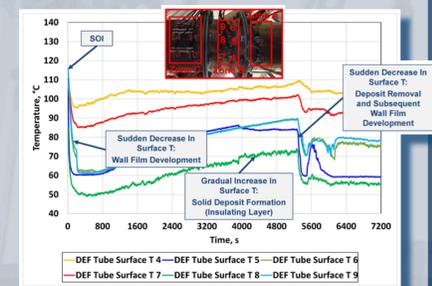


Quantitative mass trends correlation with known urea decomposition behavior



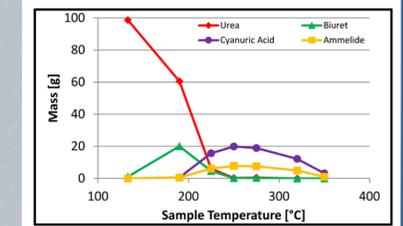
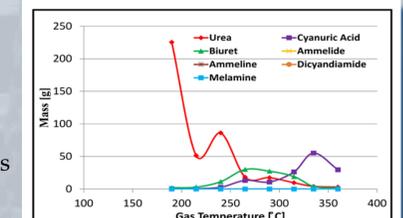
Deposits in DEF tube prior to collection

DEF injection and the exhaust pipe surface. Depending on the zone, this phenomenon was followed by a sudden decrease in temperature that was a result of deposit removal, exposing the exhaust pipe to the hot gas and subsequent wall film development.



Temperature behavior in Zone B during 190°C urea deposit test

A new validated analytical method was applied for analyses of the extracted portion of deposits. All of the urea-related target compounds were detected at a broad range of concentrations (from 91% to 0.35 ppm).



Comparison of experimental data (top) with TGA Data presented in literature (bottom) [Schaber, P. et. al., "Thermal Decomposition (Pyrolysis) of Urea in an Open Reaction Vessel," Thermochimica Acta 424, 2004]

Only deposits collected at the lowest temperatures (190°C–240°C), were completely soluble; the rest of the samples had sufficient amounts of insoluble compounds. A series of experiments with acid and basis hydrolyses confirmed the presence of oligomers in deposits forming at high temperatures.

Conclusions

Major project objectives were met during this program.

- A validated method was applied for the analyses of deposits collected at different exhaust temperatures. Results demonstrated sufficient changes in chemical composition depending on temperature.
- Observations of decrease and increase in surface temperature provided a valuable tool for development of urea injection strategies.
- A new analytical method was successfully applied for PM on two types of the filters commonly used by engine developers. Cyanuric acid and ammelide were detected on all of the filters generated during the individual test cycles, thus increasing overall PM mass. This successful application filled an existing gap in particulate characterization.

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