

# Low Temperature Urea Decomposition Phenomena in SCR Systems

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## **Objectives**

- Evaluate emissions from a CIDI engine that utilizes advanced SCR system technology.
- Elucidate urea decomposition effects on performance.

## **Approach**

- Utilize prototype SCR catalysts and a Mercedes 1.7L CIDI engine to study emissions reductions that can be achieved with the SCR technology.
- Measure both regulated and unregulated emissions, focusing on temperatures lower than 300 °C.
- Utilize engine controls and catalysts of differing size to investigate potential impacts on the effectiveness of the SCR system.

## **Accomplishments**

- Acquired the necessary catalysts (SCR and oxidation) as well as key urea injection hardware from industry partners. Installed hardware on the Mercedes 1.7L engine at ORNL for experimentation.
- Conducted numerous experiments to investigate low-temperature urea decomposition and SCR performance using engine controls to maintain space velocity and NO<sub>x</sub> concentration while varying exhaust temperature.
- Demonstrated that urea decomposition upstream of the SCR catalyst is insignificant at temperatures less than 300°C.
- Showed that ammonia storage and SCR performance are adversely impacted by urea decomposition on the catalyst surface in the first 3 inches of length of the SCR catalyst.

## **Future Directions**

- This project has reached completion. No further work is anticipated for this project in FY05.

## **Introduction**

Stationary engines and other NO<sub>x</sub> sources have been using ammonia and urea based SCR systems for many years (1). Urea SCR utilizes added urea in combination with a specifically-formulated catalyst to accomplish NO<sub>x</sub> reduction. The urea ideally breaks down to form ammonia, NH<sub>3</sub>, the

reductant utilized in reactions with  $\text{NO}_x$  (2, 3, 4, 5, 6). Handling anhydrous  $\text{NH}_3$  requires extreme caution, and would not be practical for automotive applications, although it is used in some stationary applications. Urea is a crystalline powder that is usually introduced to the exhaust stream as a solution 32.5% by weight with water. Since this technology only requires enough reductant to treat the amount of  $\text{NO}_x$  being produced, the amount of urea injected into the exhaust stream is very small. Injecting a solution of urea in water is, at present, more convenient than metering the solid form.

The complete decomposition of urea takes place in three steps. The water in the solution is first evaporated releasing the urea. The urea then decomposes to release one  $\text{NH}_3$  molecule plus one isocyanic acid (HNCO) molecule. The next step is for the HNCO to decompose to release a second  $\text{NH}_3$  molecule and one  $\text{CO}_2$  molecule (2, 3, 4, 5, 6). The two  $\text{NH}_3$  molecules are then available for  $\text{NO}_x$  reduction. There are ample opportunities in this process for non-ideal behavior, such as the incomplete decomposition of HNCO, trimerization of the HNCO to form cyanuric acid as well as other reactions that sequester the  $\text{NH}_3$  as undesirable compounds (2, 3, 5, 7).

Urea decomposition does not reach completion in the gas phase at temperatures that are typical for light-duty diesel exhaust (below 300 °C). In fact, only about 20% or less of the urea decomposes to HNCO and  $\text{NH}_3$  in the gas phase at 330 °C, and only about 50% decomposes at 400 °C (2, 3). HNCO has been shown to be very stable in the gas phase, requiring an oxide surface to catalyze its decomposition to  $\text{NH}_3$  (9). Since the HNCO is half of the initial decomposition of urea, only about 25% of the desired  $\text{NH}_3$  is available at the catalyst inlet at 400 °C. Very nearly all of the urea decomposition for low-temperature conditions will occur on the surfaces of the SCR catalyst. It is unclear how much impact these competing reactions have on the performance of the SCR catalyst under these conditions. A much better understanding of these effects is needed for identifying potential SCR catalyst improvements and for improving model-based controls for automotive SCR systems.

## **Approach**

A Mercedes 1.7-liter displacement direct-injection diesel engine at ORNL was utilized as a platform for this research. The engine was equipped with prototype catalysts provided by an industry partner. A second industry partner provided key urea injection hardware and guidance in its incorporation into the research platform. A flexible engine control system provided a means to sweep the exhaust temperature while constraining both the exhaust mass flow rate and  $\text{NO}_x$  concentration to near-constant values. SCR catalysts were evaluated by placing catalysts of two different sizes (76-mm length and 152-mm length) into the exhaust stream.

A number of both steady-state and transient measurements were conducted to determine the effects caused by urea decomposition on the SCR catalyst. Engine conditions were determined that provided appropriate conditions at the SCR catalyst inlet.  $\text{NO}_x$  concentration was held at 200 +/- 20 ppm for all but the lowest temperature conditions. The exhaust gas flow rates were held at approximately 1.1 standard cubic meters per minute (SCMM). This flow rate results in an SCR catalyst space velocity of approximately 25,000 hr<sup>-1</sup> for the 152-mm long monolith and approximately 50,000 hr<sup>-1</sup> for the 76-mm long monolith. It is important to note that in both cases the gas velocities were the same for all of the data points; only the catalyst length was changed. The catalyst inlet temperature was varied between approximately 160 °C and 250 °C for data collection while maintaining the  $\text{NO}_x$  concentration and gas velocity setpoints. Measurements of several regulated and unregulated exhaust constituents were measured at each condition. The resulting data were analyzed to deduce overall system performance and the impact of low-temperature urea decomposition.

## **Results**

Results from other studies have indicated that SCR system performance is best when the  $\text{NO}_x$  is composed of a 1:1 ratio of  $\text{NO}_2$  to  $\text{NO}$ . The oxidation catalyst in this case was found to convert  $\text{NO}$  to  $\text{NO}_2$  at high effectiveness for most conditions. This resulted in  $\text{NO}_2/\text{NO}$  ratios in excess of 1:1, sometimes in excess of 4:1 at a  $25,000 \text{ hr}^{-1}$  space velocity. (See Figure 1.)  $\text{NO}$  to  $\text{NO}_2$  conversion was not specifically investigated for other space velocities, but some data showed that the conversion efficiency was very sensitive to the space velocity. These high  $\text{NO}_2/\text{NO}$  ratios lead to  $\text{N}_2\text{O}$  formation during the SCR process. Comparisons between the 76-mm long catalyst and the 152-mm long catalyst and comparisons between use of urea and ammonia as injected reductants showed that  $\text{N}_2\text{O}$  production was higher for the 76-mm long monolith when urea was injected compared with ammonia injection. This suggests that the urea decomposition process may interfere with the SCR process in a way that results in higher selectivity to  $\text{N}_2\text{O}$  formation.

$\text{N}_2\text{O}$  emissions were examined for both SCR catalysts. The  $\text{N}_2\text{O}$  emissions were found to be higher for both the 152-mm and 76-mm catalysts when urea was injected compared with  $\text{NH}_3$  injection. The data show that injection of urea causes an increased selectivity of the SCR process in a high- $\text{NO}_2$  environment towards formation of  $\text{N}_2\text{O}$ .

Urea and ammonia injection experiments also shed light on  $\text{NH}_3$  storage in the SCR catalyst. Transient experiments conducted at several temperatures with  $\text{NH}_3$  and urea as injected reductants showed that the apparent  $\text{NH}_3$  storage capacity of the SCR catalyst was lower when urea was injected. An example of this behavior is shown in Figure 2.  $\text{NH}_3$  slip was always noted to occur at longer time periods when  $\text{NH}_3$  was injected in lieu of urea. The 76-mm SCR catalyst always exhibited  $\text{NH}_3$  slip at times significantly less than half the slip times for the 152-mm catalyst. This showed that the urea injection and decomposition process was having a negative impact on the ability of the first 76-mm of SCR catalyst in terms of its ability to store  $\text{NH}_3$ . Small amounts (less than 10 ppm) of  $\text{HCN}$  were observed just prior to and during slip of  $\text{NH}_3$ . The  $\text{HCN}$  concentration was found to be strongly correlated with  $\text{NH}_3$  concentration, and were higher when urea was injected compared with  $\text{NH}_3$  injection. No evidence of isocyanic acid emissions was observed.

## **Conclusions**

- $\text{NH}_3$  storage on the first 76-mm of SCR catalyst is reduced significantly compared with the second 76-mm when urea is injected as a reductant compared with  $\text{NH}_3$  injection.
- More  $\text{N}_2\text{O}$  is formed for over-oxidized cases when urea is injected compared with  $\text{NH}_3$  injection.
- $\text{HCN}$  formation and emission is observed just prior to  $\text{NH}_3$  slip.  $\text{HCN}$  concentration is generally proportional to  $\text{NH}_3$  concentration, but remains below 10 ppm.  $\text{HCN}$  emissions are higher when urea is injected compared with  $\text{NH}_3$  injection.

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### **FY 2004 Publications/Presentations**

1. "Decomposition Phenomena of Urea in SCR Systems", Presented at the 10<sup>th</sup> Diesel Engine Emissions Reduction (DEER) Workshop, Coronado, California, 2004.
2. "Experimental Speciation of Urea SCR Exhaust", Presented at the 7<sup>th</sup> CrossCut Lean Engine Emissions Reduction Simulation (CLEERS) Workshop, Dearborn, Michigan, 2004.
3. "Low Temperature Urea Decomposition and SCR Performance", Draft submitted for publication at the 2005 Society of Automotive Engineers Congress and Exposition, Detroit, 2005.

### **Figure Captions**

Figure 1. NO<sub>2</sub>/NO ratio entering the SCR catalyst as a function of temperature.

Figure 2. Example of N<sub>2</sub>O and NH<sub>3</sub> emissions from the 76-mm SCR catalyst during transients.