

# Effect of Unburned Methyl Esters on the NO<sub>x</sub> Conversion of Fe-Zeolite SCR Catalyst

Aaron Williams, Matt Ratcliff, Dan Pedersen and Robert McCormick  
National Renewable Energy Laboratory

Giovanni Cavataio and Justin Ura  
Ford Motor Company

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## ABSTRACT

Engine and flow reactor experiments were conducted to determine the impact of biodiesel relative to ultra-low-sulfur diesel (ULSD) on inhibition of the selective catalytic reduction (SCR) reaction over an Fe-zeolite catalyst. Fe-zeolite SCR catalysts have the ability to adsorb and store unburned hydrocarbons (HC) at temperatures below 300°C. These stored HCs inhibit or block NO<sub>x</sub>-ammonia reaction sites at low temperatures. Although biodiesel is not a hydrocarbon, similar effects are anticipated for unburned biodiesel and its organic combustion products. Flow reactor experiments indicate that in the absence of exposure to HC or B100, NO<sub>x</sub> conversion begins at between 100° and 200°C. When exposure to unburned fuel occurs at higher temperatures (250°–400°C), the catalyst is able to adsorb a greater mass of biodiesel than of ULSD. Experiments show that when the catalyst is masked with ULSD, NO<sub>x</sub> conversion is inhibited until it is heated to 400°C. However, when masked with biodiesel, NO<sub>x</sub> conversion is observed to begin at temperatures as low as 200°C. Engine test results also show low-temperature recovery from HC storage. Engine tests indicate that, overall, the SCR system has a faster recovery from HC masking with biodiesel. This is at least partially due to a reduction in exhaust HCs, and thus total HC exposure with biodiesel.

## INTRODUCTION

Biodiesel is a renewable fuel derived from vegetable oil, animal fat, or waste cooking oil and consists of the

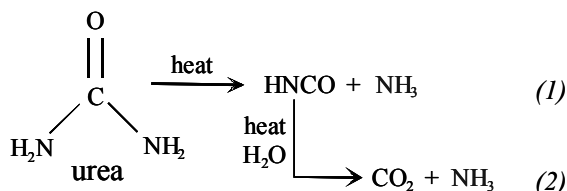
methyl esters of fatty acids. It is typically used in the United States as a diesel fuel blend component at 20 volume percent (B20) and lower. At levels up to 5 volume percent (B5), the fuel will meet the ASTM D975 diesel fuel specifications, and it can be used in any application as if it were petroleum diesel [1]. Because of the U.S. Renewable Fuel Standard (RFS), which requires 36 billion gallons of renewable fuel in 2022 [2], and an ever-increasing number of state mandates for biofuels, the use of biodiesel will become more common. With the anticipated widespread use of biodiesel it is important to fully understand biodiesel's impact on new and existing engine and emission control technologies.

Beginning in 2007, the U.S. Environmental Protection Agency's (EPA's) heavy-duty on-road standard for NO<sub>x</sub> emissions was lowered from 2.0 g/bhp-hr to 0.2 g/bhp-hr [3]. This 90% reduction is phased in between 2007 and 2010; engines must produce no more than 1.2 g/bhp-hr of NO<sub>x</sub> between 2007 and 2009 and 0.2 g/bhp-hr by 2010. In order to meet the 2010 standard, some form of NO<sub>x</sub> aftertreatment technology will most likely be needed. Selective catalytic reduction (SCR), with either ammonia (NH<sub>3</sub>) or urea, is a leading de-NO<sub>x</sub> technology, having been used in stationary applications for over two decades [4] and achieving peak reduction efficiencies of well over 90%.

In automotive exhaust conditions, urea decomposes to NH<sub>3</sub> following a well-known two-step decomposition process, as outlined in Figure 1. Step one proceeds with warm gas-phase thermolysis (Eq. 1) followed by a

further surface-phase hydrolysis reaction with water (Eq. 2). In the presence of oxygen, NO<sub>x</sub> reduction is possible due to the high selectivity of NH<sub>3</sub> to react with NO<sub>x</sub> to form elemental N<sub>2</sub> (Eq. 3-5).

#### Urea Decomposition:



#### NO<sub>x</sub> Reduction:

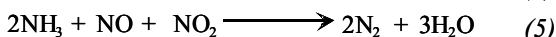
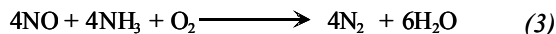


Figure 1. Urea Decomposition and NO<sub>x</sub> Reduction Reactions [5].

Both Cu-zeolite and Fe-zeolite formulations have been shown to exhibit high NO<sub>x</sub> conversion potential. The three main differences between Cu and Fe involve the activity-temperature window, NO/NO<sub>2</sub> sensitivity, and robustness to hydrocarbons [6]. Cu-zeolite formulations have higher activity below 350°C, while Fe-zeolite formulations have been shown to be more active above 350°C (for cases where the feed gas composition is 100% NO). Fe-zeolite SCR formulations require up to 50% NO<sub>2</sub> (of the total NO<sub>x</sub>) to enhance the low-temperature activity. Compared to Fe-zeolite SCR formulations, recent enhancements in Cu-zeolite SCR washcoats have shown higher tolerance to diesel soot and various types of hydrocarbons [7-9].

Previous engine testing studies have shown no measurable difference in Fe-zeolite SCR system performance for B20 relative to ULSD in the range of 300° to 540°C [10-13]. However, under normal operating conditions, the system will experience a significant period of time below 300°C. Previous research conducted at Ford has shown that certain Fe-zeolite SCR catalyst formulations have the ability to adsorb and store unburned hydrocarbons (HC) below 300°C. These stored HCs block NO<sub>x</sub> reaction sites and lower overall system performance. Furthermore, the type of unburned HCs (paraffins, olefins or aromatics) were shown to have different impacts on the storage and masking effect [8].

The objective of this study is to investigate how biodiesel and exhaust HC generated from the combustion of biodiesel affect Fe-zeolite SCR catalyst performance in comparison to ULSD. This was accomplished through a combination of engine and flow reactor experiments.

## EXPERIMENTAL SETUP

**ENGINE AND AFTERTREATMENT SYSTEM** – The engine test setup consisted of a 2002 model year 5.9 L 300 hp Cummins ISB. Properties of the test engine are shown in Table 1. The engine employed cooled high-pressure exhaust gas recirculation (EGR), a variable geometry turbocharger, electronic control, and high-pressure common rail direct fuel injection, designed and calibrated to meet the 2004 U.S. heavy-duty emissions standards. The engine was mounted to a DC electric engine dynamometer at NREL's Renewable Fuel and Lubricants (ReFUEL) laboratory.

Table 1. Test Engine Specifications

| Cummins ISB       |                    |
|-------------------|--------------------|
| Serial Number     | 56993170           |
| Displacement      | 5.9 L              |
| Cylinders         | 6                  |
| Rated Power       | 224 kW @ 2500 rpm  |
| Rated Torque      | 895 N-m @ 1600 rpm |
| Bore x Stroke     | 10.2 x 12 cm       |
| Compression Ratio | 16.5:1             |
| Fuel System       | Common Rail        |

The engine was retrofitted with a diesel particle filter (DPF) followed by a selective catalytic reduction (SCR) system. The DPF was a 12.5 L (22.9 cm diameter x 30.5 cm length) uncatalyzed, wall flow DPF. This system generally uses an oxidation catalyst upstream of the DPF for NO<sub>2</sub> formation used in soot oxidation. However, for the purposes of this testing, the diesel oxidation catalyst (DOC) was removed to accelerate the rate of HC adsorption onto the SCR system. The DPF was mounted 152 cm from the engine turbo flange outlet.

The SCR system comprised two 7.2 L (24.1 cm diameter x 15.2 cm length) Fe-zeolite catalyst bricks. The system used air-assisted aqueous urea injection, with an injector mounted 70 cm upstream of the SCR catalyst. An ammonia slip catalyst was placed downstream of the SCR for cleanup of unconsumed ammonia. The SCR was mounted 98 cm from the outlet of the DPF.

Sample probes for NO<sub>x</sub> and total hydrocarbon (THC) measurement were placed at the engine-out, DPF-out and SCR-out positions. The overall setup and relative location of all instrumentation is illustrated in Figure 2. In addition, engine and emissions sampling systems were instrumented for measurement of all other critical temperatures and pressures.

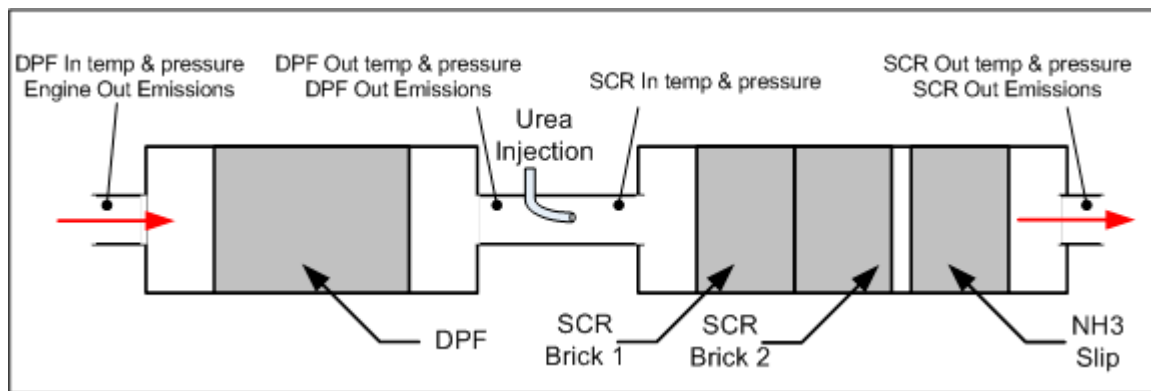


Figure 2. Aftertreatment system for engine experiments.

testing was carried out on the outlet segments (see Figure 3, top right) of the brick 1 cores.

Raw exhaust gas emissions were measured with two Horiba chemiluminescence detection analyzers for  $\text{NO}_x$  and a single Horiba flame ionization detection analyzer for THC.

An additional engine-out sampling probe was used to collect exhaust gas samples for hydrocarbon speciation. Evacuated, 3.2 L Silonite™ coated canisters were connected to this probe and filled with exhaust gas during steady-state operation. These samples were analyzed by gas chromatography-mass spectrometry (GCMS) using a system composed of an Agilent 6890/5975B GCMS and an Entech 7100A inlet-preconcentrator. A cold trap dehydration method was used in concentrating 200 mL aliquots of exhaust gas to remove permanent gases and water. The concentrated hydrocarbons were automatically injected into the GCMS and separated on a 60 m Restek Rxi™-1 ms column.

Test fuels included a 2007 Certification ultra-low-sulfur diesel (ULSD) and a neat biodiesel (B100) derived from a soy feedstock. The soy biodiesel was S15 grade and met the requirements of ASTM D6751. While biodiesel is typically used as a blend with petroleum diesel, here we use B100 to magnify any effects of biodiesel on catalyst performance. The properties of the ULSD and B100 employed are listed in Appendix 1.

**CATALYST CORE SAMPLES** – At the completion of engine testing, the Fe-zeolite catalyst bricks were sent to Ford for use in the flow reactor studies. Multiple 1-in. diameter cores were drilled out of each of the two catalyst bricks. These cores were further dissected into 1-in. (diameter) x 1-in. (length) samples to be used in the flow reactor. As shown in Figures 3 and 4, the first brick appeared to be coated with an adsorbed HC or particulate matter resulting from previous engine operation. These samples were first baseline tested and then fully regenerated to remove the adsorbed matter in preparation for flow reactor studies. All flow reactor

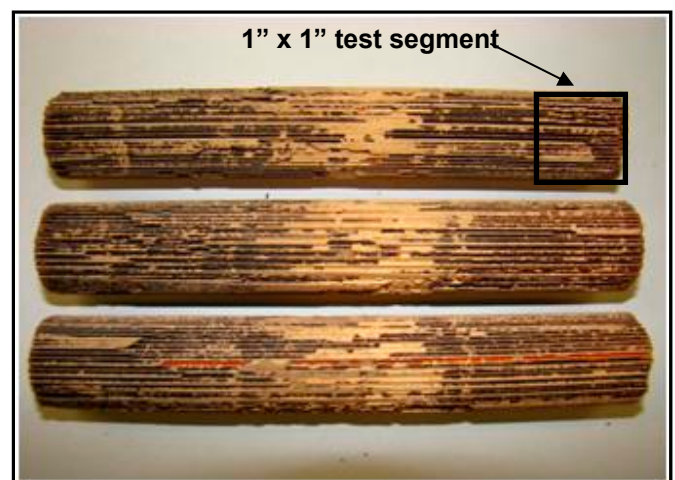


Figure 3. Brick one catalyst cores.



Figure 4. Brick two catalyst cores.

**FLOW REACTOR SYSTEM** – A bench flow reactor was used to simulate low-temperature and high-temperature hydrocarbon masking. Figure 5 illustrates the laboratory apparatus utilized for this purpose. Fuel saturation and  $\text{NO}_x$  activity measurements for the 1.0-in. diameter x 1.0-in. long Fe-zeolite SCR catalysts were performed in a quartz flow reactor connected to a MIDAC FTIR system.