

Understanding System- and Component-Level N₂O Emissions from a Vanadium-Based Nonroad Diesel Aftertreatment System

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ABSTRACT

Nitrous oxide (N₂O), with a global warming potential (GWP) of 297 and an average atmospheric residence time of over 100 years, is an important greenhouse gas (GHG). In recognition of this, N₂O emissions from on-highway medium- and heavy-duty diesel engines were recently regulated by the US Environmental Protection Agency (EPA) and National Highway Traffic Safety Administration's (NHTSA) GHG Emission Standards. Unlike NO and NO₂, collectively referred to as NO_x, N₂O is not a major byproduct of diesel combustion. However, N₂O can be formed as a result of unselective catalytic reactions in diesel aftertreatment systems, and the mitigation of this unintended N₂O formation is a topic of active research. In this study, a nonroad Tier 4 Final/Stage IV engine was equipped with a vanadium-based selective catalytic reduction (SCR) aftertreatment system. Experiments were conducted over nonroad steady and both cold and hot transient cycles (NRSC and NRTC, respectively). Engine-based results show that N₂O emissions for this nonroad engine and aftertreatment system are below the current 0.1 g/bhp·hr on-highway GHG standard. To better understand the processes which contribute to the system-level N₂O emissions seen during engine testing, reactor-based experiments were conducted to elucidate the fundamental component-level mechanisms responsible for N₂O formation. This study provides significant system- and component-level insights into the formation of N₂O in diesel aftertreatment systems.

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INTRODUCTION

Diesel engines are an important source of power for the world's passenger cars, trucks, and freight and cargo industries, but they are also a source of significant emissions. A component of these emissions, nitrous oxide (N₂O) is a greenhouse gas (GHG) with a global warming potential (GWP) of 297 in comparison to carbon dioxide (CO₂). The U.S. Environmental Protection Agency (EPA) reported that approximately 5% of the 2013 greenhouse gas emissions in the U.S. could be attributed to N₂O. While the majority of these emissions are derived from the agriculture industry (synthetic fertilizer application), the transportation industry is responsible for roughly 5% of the U.S.' N₂O emissions [1]. For this reason, N₂O continues to be regulated by the Phase 2 Greenhouse Gas Emissions Standards promulgated by the U.S. EPA and the U.S. National Highway Traffic and Safety Administration (NHTSA). Permissible emissions of N₂O are capped at 0.1 g/bhp·hr for on-highway engines [2]. While this level remains unchanged in comparison to the Phase 1 GHG Emissions Standard, the authors make it clear that additional, future reductions in N₂O are likely.

Unlike NO and NO₂, both of which form during and survive diesel combustion, engine-out emissions of N₂O are minimal. Several sources have published N₂O emissions factors for heavy-duty diesel engines without aftertreatment [3, 4, 5]. Graham et al. have suggested an N₂O emission factor of 0.023 g_{N2O}/L_{diesel}, while Lipman et al. propose a factor between 0.02 and 0.09 g_{N2O}/mile [3, 4]. More

recently, the U.S. EPA has published an emissions factor of 0.0048 g_{N2O}/mile [5]. On the other hand, the post-combustion catalytic formation of N₂O is possible in aftertreatment systems designed to treat emissions from internal combustion engines [3, 6]. Graham et al. have reported emissions from a variety of on-highway light- and heavy-duty diesel engines operating with aftertreatment [3]. Based on emissions measurements, the authors proposed emission factors of 0.047 and 0.064 g N₂O /L diesel for engines operating with a diesel oxidation catalyst (DOC) and a diesel particulate filter (DPF), respectively. However, the authors did not measure the impact of a selective catalytic reduction (SCR) or ammonia oxidation (AMOX) catalyst. More recently, Kamasamudram et al. have summarized the formation of N₂O over various catalysts using reactor-based methods [6]. In alignment with the work of Graham et al., the authors found that N₂O forms over DOC aftertreatment components. In addition, N₂O formation was reported over Cu-zeolite selective catalytic reduction (SCR) catalysts, vanadium-based SCR catalysts, and AMOX catalysts. It was reported that N₂O formation is formulation specific within a certain technology (e.g., Cu-zeolite SCR catalysts), and that some exhaust conditions favor formation more than others.

The present study improves upon the current knowledge related to component and system level N₂O formation in diesel aftertreatment systems. Engine-based experiments are conducted with a U.S. Tier 4 Final/EU Stage IV-compliant diesel engine. In addition, the vanadium-based aftertreatment system was evaluated, and N₂O

emissions are reported for nonroad transient and steady-state cycles. Transient emissions are reported for both cold- and hot-start. Engine emissions and component-level reactor-based results are then used to determine real-world N_2O formation mechanisms.

EXPERIMENTAL

Engine and Aftertreatment

An 8.9 liter Cummins QSL engine rated at 380 HP (283 kW) was used for this study (see [Table 1](#) for engine properties). The engine was turbocharged and charge air cooled with electronically controlled high pressure common rail fuel injection and cooled exhaust gas recirculation. This engine is intended for industrial nonroad U.S. Tier 4 Final and EU Stage IV applications and is designed for use with ultra-low-sulfur diesel (ULSD) fuel. The engine was operated with BP #2 ULSD fuel (detailed properties found in [Table 2](#)) and Valvoline Premium Blue 15W-40 lubrication oil, and was equipped with an open crankcase ventilation system (OCV).

Table 1. Engine properties

Configuration	Inline-6
Displacement	8.9 liter
Bore	4.49 in (114 mm)
Stroke	5.69 in (145 mm)
Max. Power at rpm	400 hp (298 kW) at 1900
Max. Torque at rpm	1200 ft-lb (1627 N-m) at 1500

Table 2. Test fuel properties

Fuel Property	Value
Net Heat of Combustion	45.6 MJ/kg
API Gravity	36
Cetane Index	47.4
Sulfur Content	6 ppm
Di-aromatics %m/m	2.2 %m
Tri+-aromatics %m/m	0.3 %m
Poly-aromatics %m/m	2.5 %m
Total aromatics %m/m	26.3 %m
Distillation Properties	
Initial Boiling Point	179°C
10%	214°C
50%	260°C
90%	323°C
End Point	352°C

The aftertreatment system evaluated in this study consisted of a V-SCR catalyst followed by an AMOX catalyst. The catalysts are state-of-the-art, and their sizes are typical of commercial components for this engine with a maximum SCR gas hourly space velocity in this study of approximately $80,000 \text{ hr}^{-1}$. The dual-layer AMOX catalyst consists of both a platinum group metal (PGM) and an SCR layer. It should be noted that this aftertreatment system and its respective controls logic were not optimized for this engine, and the system-level emissions shown in this study should not be assumed to represent those of a certified configuration. However, the mechanisms and trends discussed herein are representative of those from a certified configuration.

Sampling Protocol

Engine exhaust was mixed with purified, humidity- and temperature-controlled dilution air in a constant volume sampling (CVS) dilution tunnel. A detailed explanation of the design, operating principles, quality assurance and quality control (QA/QC) procedures for the CVS dilution tunnel and complete source dilution sampling system (SDS) is provided by Liu et al. [7]. The CVS dilution tunnel was operated at a nominal flow rate of 2250 standard cubic feet per minute (SCFM) (64.7 standard cubic meters per minute), resulting in average primary dilution ratios ranging from 4.3 to 5.3, depending on the test cycle. Dilute N_2O measurements were made with a MKS 2030 HS Fourier transform infrared (FTIR) spectrometer connected to the dilution tunnel with a heated sample line designed to maintain the exhaust gas sample at 191°C. In addition, all FTIR calibrations were derived for gas-phase measurement at 191°C.

Test Cycles and Procedure

N_2O emissions from the V-SCR aftertreatment system were measured over both the transient and steady-state engine dynamometer test-cycles required by the EPA Tier 4 Final standards for nonroad compression-ignition engines. The nonroad transient cycle (NRTC) “provides a representation of a broad range of nonroad diesel equipment activity” and is a composite of application duty cycles based on the following nonroad applications [8]:

- A. Backhoe Loader
- B. Wheel Loader
- C. Crawler Tractor
- D. Agricultural Tractor
- E. Excavator
- F. Arc Welder
- G. Skid Steer Loader

The ISO 8178 test cycle, in its 8-mode, C1 schedule, applies to nonroad vehicles and industrial equipment and simulates intermittent engine use at various steady-state operating conditions between idle and rated power. This cycle is also referred to as the nonroad steady cycle (NRSC). Plots of engine speed and torque for these two test cycles are presented in [Figures 1](#) and [2](#).

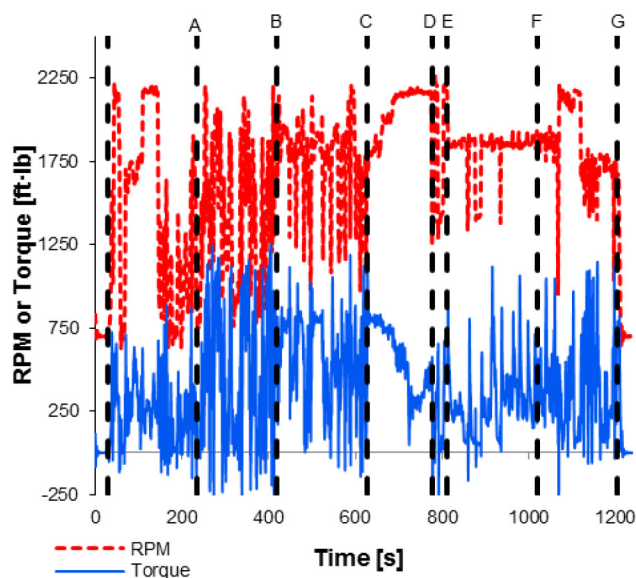


Figure 1. NRTC RPM and torque with end times of application duty-cycles indicated

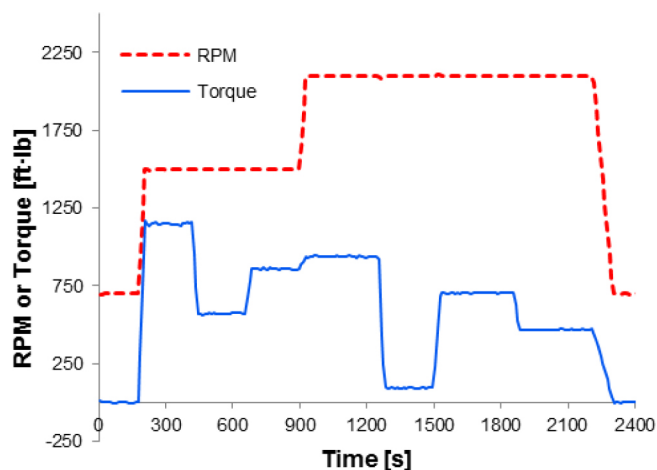


Figure 2. NRSC RPM and torque

Each steady-state run consisted of a 40-minute NRSC cycle with a prior NRTC conditioning cycle to bring the engine and aftertreatment system to a repeatable starting temperature. The duration of steady-state runs was selected to achieve optimal sample media mass loadings. The transient NRTC was run four times per sample, with one cold and three hot starts. Between the cold and hot tests, there was a 20-minute soak period during which the engine was shut off and sampling was suspended. Overnight engine cool downs were used to ensure initial temperatures of the system were between 20 and 25°C for the cold start.

Catalyst Reactor

A catalyst core-reactor was used to further study the formation of N_2O over the individual catalyst components evaluated during the engine-based testing. A schematic of the system is presented in Figure 3. The core-reactor used in this study consists of MKS™ mass flow controllers for gas metering, a Waters™ high performance liquid

chromatography pump for water introduction, a Bronkhorst™ vapor delivery system for introduction of $C_{12}H_{26}$ (not included in the present study), a Lindberg™ 3-zone tube furnace for reactor temperature control, and a MKS 2030 HS FTIR spectrometer for gas analysis. All lines are heated to approximately 190°C to eliminate condensation of water vapor and hydrocarbons. In addition, all FTIR calibrations were derived for gas-phase measurement at 191°C. The quartz reactor tubes used in this study were 39 inches (90 cm) long with inner and outer diameters of 1.1 inches (28 mm) and 1.26 inches (32 mm), respectively. The inlet 10 inches (25.4 cm) of the reactor were filled with 4 mm quartz beads to ensure that incoming gas is uniformly mixed and heated. All gases used in this study were provided by Airgas. Pure gases N_2 and O_2 were Ultra High Purity grade (99.999%), while two component NO and NH_3 mixtures in N_2 were National Institute of Standards and Technology (NIST) traceable Primary Standards.

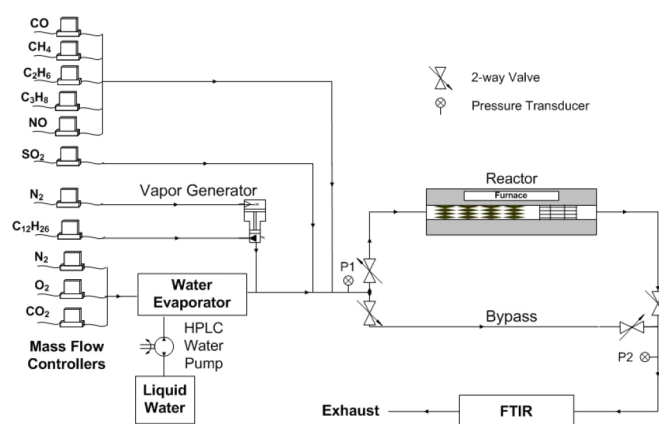


Figure 3. Schematic of catalyst core-reactor.

RESULTS AND DISCUSSION

Engine-based Emissions

Brake-specific N_2O emissions are reported for the V-SCR aftertreatment system for NRSC, cold-start NRTC (NRTC_cold), and hot-start NRTC (NRTC_hot) cycles in Figure 4. All values are the average of at least three runs ($n \geq 3$), and error bars represent standard error. In all cases, emissions are significantly lower than the on-highway, heavy-duty regulated limit of $0.1 \text{ g}_{N_2O}/\text{bhp}\cdot\text{hr}$. For reference, engine-out (EO) emissions are less than $0.02 \text{ g}_{N_2O}/\text{bhp}\cdot\text{hr}$ for the three cycles. While N_2O forms from the interaction of oxygen radicals and molecular nitrogen during diesel combustion processes, the majority of any combustion-derived N_2O decomposes to NO via the well documented N_2O pathway as a result of the high temperatures and pressures of conventional diesel combustion [9]. For other combustion regimes, such as Homogeneous Charge Compression Ignition (HCCI), it has been reported that N_2O is likely to be present in exhaust [10]. The increase in N_2O emissions resulting from V-SCR aftertreatment, in comparison to engine-out, has been previously reported by Graham et al. for engines operating with DOC and DPF catalysts [3].