

N₂O Emissions of Low Emission Vehicles

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ABSTRACT

The Environmental Protection Agency (EPA) and Department of Transportation's National Highway Traffic Safety Administration (NHTSA) have finalized regulation that will reduce greenhouse gases and increase fuel economy for model year (MY) 2012-2016 light-duty vehicles. This ruling not only includes a CO₂ standard that will require vehicles to achieve fleet average 35 mpg by MY 2016, but will apply a cap on nitrous oxide (N₂O) and methane emissions to 10 and 30 mg/mile, respectively, however CO₂ emission reductions can be exchanged for either N₂O or methane credit. The work outlined investigates the N₂O emissions of a variety of low emission vehicles per the Federal Test Procedure (FTP). Fourier Transform Infrared Spectroscopy (FTIR) was used to measure both bag and modal N₂O emissions. N₂O emissions were less than 1 mg/mile for three SULEV vehicles with 6,400 km aged catalysts. For 240,000 km equivalent dynamometer aged catalyst systems, N₂O emissions varied from 1.3 to 8 mg/mile on various low emission vehicles. Both close-coupled and underfloor catalysts can generate N₂O emissions especially during the cold and warm engine starts. Most catalysts stop generating N₂O when catalyst temperatures exceed 450°C. However steady-state production of N₂O was observed at 550°C. Fast light-off strategies appear to minimize N₂O emissions. Turbocharged vehicles with lower catalyst bed temperatures generate greater amounts of N₂O emissions. This work will also show that catalyst technology can effect tailpipe N₂O emissions.

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INTRODUCTION

N₂O emissions in recent years have gained increased notoriety, not only for its use in medicine, dentistry, food industry, and fast cars; but also its impact to the climate. N₂O, along with methane (CH₄) and carbon dioxide (CO₂), are included in the list of regulated emissions known as greenhouse gases (GHG). It has been reported that N₂O at lower atmospheric temperatures can reside in the atmosphere up to 130 years (120 ± 30). Such longevity in a 100 year time span compared to CO₂, makes N₂O per molecule, 296 times higher in global warming potential (GWP) [1]. Past work from the 2005 Canadian and United States GHG national inventories, report that 88% of the N₂O emissions from road transportation for both countries are attributable to on-road gasoline vehicle sources [2]. This makes N₂O second only to CO₂ as the largest contributors to GHG inventories.

In 2010, the Environmental Protection Agency (EPA) and the Department of Transportation's National Highway Traffic Safety Administration (NHTSA) announced regulations for GHG based on their impact to the climate such as described

above. The Code of Federal Regulations [3] states all MYs 2012 - 2016 vehicles shall comply with a limit of 10 mg/mile for N₂O and 30 mg/mile for CH₄ at full useful life, as measured per the Federal Test Procedure (FTP). Additionally, as an option to meeting the N₂O and CH₄ standards, manufactures can decide to include both in their Carbon Related Exhaust Emissions (CREE) fleet averages [4].

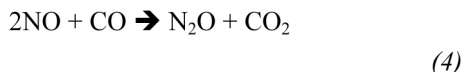
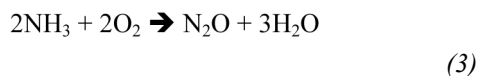
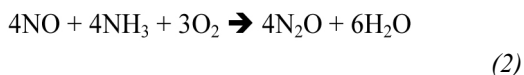
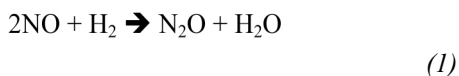
Even though previous emissions standards only required the measurement of "NO_x" (which is a total account for both nitric oxide (NO) and nitrogen dioxide (NO₂) for emission certification and for surveillance compliance), previous studies have been completed measuring N₂O. It is reported that some of the earliest measurements of N₂O from automotive exhaust were performed in the 1970 to early 1980's timeframe. This was done to further understand the impact of employing catalytic converters [1]. Results from these early and later studies indicate that N₂O production resulted as a byproduct from catalytic reactions and that non-catalyst treated exhaust contained low levels in comparison (5 mg/mi compared to > 10 mg/mile). N₂O values ranged from

29 mg/mi for vehicles equipped with oxidation catalysts, 61 mg/mi for dual-bed catalysts, and 45 mg/mi for vehicles equipped with three way catalysts (TWC).

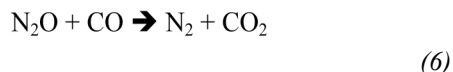
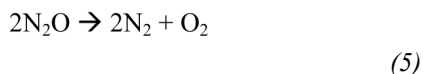
As standards for lower emission levels were enforced, this drove advances in newer vehicle emissions technologies to be used which resulted in lowered N₂O emissions. This downward trending of N₂O emissions was further illustrated from published data in 2004 for certification categories ranging from Tier 0 to Super Ultra Low Emission Vehicles (SULEV) [1]. The average N₂O FTP emissions were 5 mg/mi for ULEV vehicles and 1 mg/mi for SULEV vehicles with the use of California Phase II gasoline.

Real-time data showed that N₂O emissions were primarily formed during the early period of catalyst light-off, and declined significantly as the catalyst reached its equilibrium temperature [1]. Additionally, results from other studies further indicated that N₂O emissions from light-duty (LD) gasoline vehicles were heavily dependent upon several factors. These factors included exhaust catalyst technologies, precious metal concentrations, catalyst aging, fuel sulfur level, driving cycles, ambient conditions, and catalyst operating temperatures [5, 6, 7]. Here too, it is important to note that along with more stringent emission levels came standards for lower sulfur levels in fuel.

To understand N₂O formation from a chemical perspective, study of the formation mechanisms have been completed. Essentially no net N₂O formation is from the internal-combustion process (i.e. engine) [6]. Therefore, N₂O is predominately produced across exhaust catalysts. The following reactions are proposed for N₂O production [6, 8]:



N₂O may also be decomposed by catalysts at higher temperatures typically over 350°C [5, 6]:



N₂O formation over individual rhodium (Rh), platinum (Pt) and palladium (Pd) catalysts and their combinations has been studied [8, 9, 11]. Rh and Pt catalysts gave N₂O at lower temperature region (250°C - 400°C), while Pd catalyst generated N₂O through 500°C. Rh catalysts produced the largest amount of N₂O.

To further investigate N₂O production, this study focuses on measuring N₂O emissions from a selection of various emission vehicles per the Federal Test Procedures (FTP). Test vehicles range from Tier 2 Bin 8 to Partial Zero Ultra Low Emission Vehicles (PZEV). This work further complements earlier studies which mainly focused on later model year platforms and previous emission regulations [1, 2, 8, 9].

In this study, current Fourier Transform Infrared Spectroscopy (FTIR) was used to measure both bag and real time modal N₂O emissions routinely in comparison to earlier studies that measured one or the other [1, 5, 8, 10]. In addition, this study employed the use of a bag mini-dilutor (BMD) in place of the ambient diluted samples using the conventional constant volume sampler (CVS). This added the advantage of not having to resolve between very low levels of N₂O exhaust samples and ambient concentrations of N₂O.

In regards to catalysts aging, FTP evaluations were performed at 6,400 km road aging and 240,000 km equivalent engine dynamometer aging to evaluate the aging effects on N₂O production. This combination differs also from previous studies which used either field aged or engine dyno aged samples [1, 2, 5, 8, 9, 11]. Various catalyst technologies were included to study their effects as well.

EMISSION MEASUREMENTS

Prior to emission testing, test vehicles were drained and fueled with California Air Resources Board (CARB) Phase II Reformulated Certification fuel. Average sulfur content reported per the manufacturer was 33 parts per million by weight (ppmw). Each vehicle's dyno load coefficients were determined on a 48-inch single-roll Zoller electric dynamometer as per SAE J2264 - 1995. After dyno load determination, each vehicle was subjected to a preparation cycle consisting of two back-to-back FTP72 cycles followed by a US06 cycle [3]. The vehicle was then parked and allowed to soak until its temperature equalized to ambient (~22°C).

All of the emission testing was conducted per procedures of EPA Code of Regulations [3] at ~22°C in Cell 252 at Umicore Autocat USA in Auburn Hills, MI. N₂O measurements were conducted using an AVL SESAM 4 Fourier Transform Infrared Spectrometer (FTIR). The spectrometer is supplied by MKS and is a high resolution instrument (0.5 cm⁻¹) [12]. It acquired data at a 5Hz sample rate with a sample flow of 5 to 10 L/min. At this sample rate, it is reported the typical minimal detectable concentration (MDC) for N₂O is 0.5 ppm. In-house investigation matched this finding using the same calculation method [13]. To validate measurement accuracy, samples of a ±1% standard gas of N₂O/N₂ (traceable to NIST) were measured undiluted and diluted respectively (195, 19.5, 9.75 ppm). Results have shown a 1.6% difference from the stated value at 195 ppm, a

2.45% difference at the diluted value of 19.5 ppm, and 2.21% at 9.75 ppm.

All modal N₂O measurements were acquired in unison with the other regulated emissions with a heated (191°C) perfluoroalkoxy (PFA) sample line. Diluted bag N₂O measurements were performed at the end of the test cycles using a BMD equipped with Kynar sample bags. This device is EPA approved for low level diluted bag measurements, using proportional partial dilution sampling companioned with a direct vehicle exhaust (DVE) flow meter for total exhaust volume measurement.

Dilute Bag N₂O measurements were made possible from a procedure using an AVL BMD 150 that has been modified (hardware and software) to access diluted bag samples (supplied sample to FTIR at atmospheric pressure). This functionality was created for quality control measurement purposes (BMD Diagnostic) at Umicore Auburn Hills. The tailpipe vehicle raw exhaust was diluted with a constant dilution ratio of 6.51 using pure nitrogen as the diluent. Each test phase bag was measured separately with the FTIR and the data averaged to calculate the flow weighted mass. As shown in Figure 1, both raw modal and diluted bag N₂O measurements on a per phase basis were compared and showed to have very good correlation in this study.

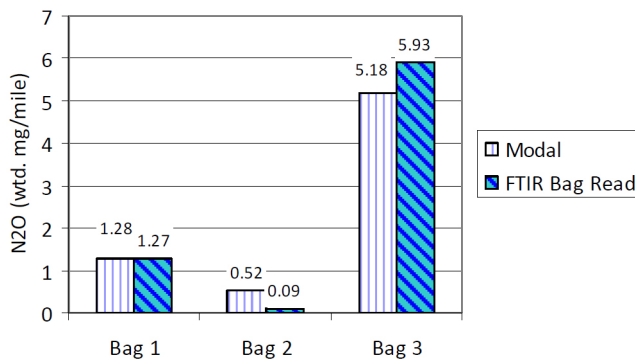


Figure 1. Bag to Modal FTIR Correlation

VEHICLES AND CATALYSTS

Table 1 summarizes the vehicles and their associated catalyst systems used in this work. All of the vehicles have SULEV calibrations with the exception of Vehicle G which has a BIN-8 calibration. SULEV vehicles E and F use secondary air injection prior to the close-coupled (CC) catalyst to facilitate catalyst light-off. Five of the vehicles have both close-coupled and underfloor(UF) catalysts, the other two vehicles E and G have only close-coupled catalyst systems. Additionally, Vehicles F and G are both turbocharged with direct injected fuel systems and their calibrations employ deceleration fuel cuts. The other vehicles are port fuel injected. Platinum Group Metals (PGM) loadings vary greatly. Vehicle C uses the most Pt, Pd and Rh of the SULEV calibrated vehicles. Conversely, SULEV Vehicle D uses the least amount of Rh.

Table 1. Vehicle and Catalyst Descriptions

Veh.	A	B	C	D	E	F	G
MY	'12	'12	'11	'10	'09	'10	'07
Engine	2.4L PFI	2.5L PFI	2.5L PFI	2.0L PFI	2.4L PFI	2.0L GTDI	1.6L GTDI
AIR Cal	No	No	No	No	Yes	Yes	No
Cal	SULEV	SULEV	SULEV	SULEV	SULEV	SULEV	Bin-8
CC Cats.	Pd (g)	3.98	3.15	9.53	3.90	5.64	3.00
	Rh (g)	0.80	0.21	0.87	0.10	0.68	0.06
	Vol (L)	1.00	0.88	0.92	1.38	2.46	0.85
							1.33
UF Cats.	Pt (g)	0.00	1.16	1.52	0.00		0.00
	Pd (g)	0.88	0.00	3.43	0.34		1.48
	Rh (g)	0.18	0.39	0.48	0.02		0.12
	Vol (L)	1.00	1.32	1.37	0.69		1.68

6,400 Kilometer Results

Vehicles A, B and C were road aged for 6,400 km and FTP emission measurements were made using California Phase-II fuel with tailpipe modal N₂O FTIR measurements. Prior to the FTP testing, the production converter system was prepped on the vehicle with two back-to-back FTP72 cycles, plus a US06 cycle then soaked. Three FTPs were then performed with 12 - 24 hr soaks in between. The average NMHC, NO_x and N₂O emissions are shown in Figure 2. Vehicles A and B are comfortably below the SULEV NMOG standard of 10 mg/mile and the 20 mg/mile standard for NO_x. Vehicle C with the highest PGM loadings is above the 10 mg/mile NMOG standard. Regarding N₂O emissions, Vehicles A and C exhibited no measureable emissions. Vehicle B N₂O emissions were < 1 mg/mile, which is well below the 10 mg/mile standard. Within this small sampling size of SULEV vehicles, N₂O emissions do not appear to be a problem with relatively fresh catalysts.

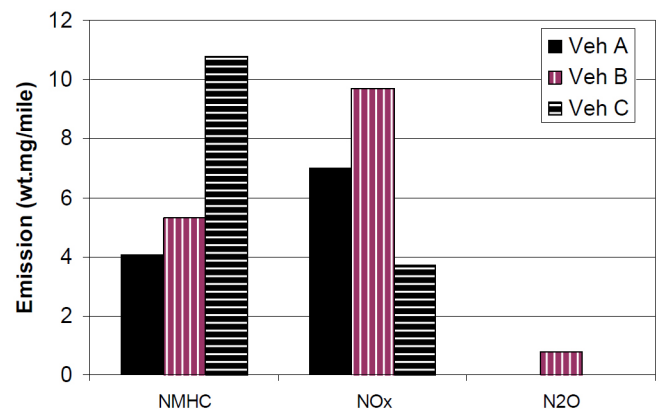


Figure 2. SULEV Vehicle 6,400 Kilometer Emissions

Aged Catalyst Results

The catalysts for Vehicles C, D, E, F and G were dynamometer aged using a 4 mode aging schedule for 100 hours, which is estimated to be equivalent to 240,000 km road aging. Peak close-coupled catalyst temperatures reached 980°C during the hot lean portion of the cycle. The underfloor catalysts were aged behind the close-coupled catalysts with a section of pipe placed in between. The pipe length duplicated the distance between the converters for the specific vehicle application. Figures 3, 4, 5, 6, 7 present the