

NMOG Emissions Characterizations and Estimation for Vehicles Using Ethanol-Blended Fuels

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ABSTRACT

Ethanol is a biofuel commonly used in gasoline blends to displace petroleum consumption; its utilization is on the rise in the United States, spurred by the biofuel utilization mandates put in place by the Energy Independence and Security Act of 2007 (EISA). The United States Environmental Protection Agency (EPA) has the statutory responsibility to implement the EISA mandates through the promulgation of the Renewable Fuel Standard. EPA has historically mandated an emissions certification fuel specification that calls for ethanol-free fuel, except for the certification of flex-fuel vehicles. However, since the U.S. gasoline marketplace is now virtually saturated with E10, some organizations have suggested that inclusion of ethanol in emissions certification fuels would be appropriate. The test methodologies and calculations contained in the *Code of Federal Regulations* for gasoline-fueled vehicles have been developed with the presumption that the certification fuel does not contain ethanol; thus, a number of technical issues would require resolution before such a change could be accomplished. This paper makes use of the considerable data gathered during the mid-level blends testing program to investigate one such issue: estimation of non-methane organic gas (NMOG) emissions. The data reported in this paper were gathered from over 600 cold-start Federal Test Procedure (FTP) tests conducted on 68 vehicles representing 21 models from model year 2000 to 2009. Most of the vehicles were certified to the Tier-2 emissions standard, but several older Tier-1 and national low emissions vehicle program (NLEV) vehicles were also included in the study. Exhaust speciation shows that ethanol, acetaldehyde, and formaldehyde dominate the oxygenated species emissions when ethanol is blended into the test fuel. A set of correlations were developed that are derived from the measured non-methane hydrocarbon (NMHC) emissions and the ethanol blend level in the fuel. These correlations were applied to the measured NMHC emissions from the mid-level ethanol blends testing program and the results compared against the measured NMOG emissions. The results show that the composite FTP NMOG emissions estimate has an error of 0.0015 ± 0.0074 g/mile for 95% of the test results. Estimates for the individual phases of the FTP are also presented with similar error levels. A limited number of tests conducted using the LA92, US06, and highway fuel economy test cycles show that the FTP correlation also holds reasonably well for these cycles, though the error level relative to the measured NMOG value increases for NMOG emissions less than 0.010 g/mile.

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INTRODUCTION

Ethanol is a biofuel commonly used in gasoline blends to displace petroleum consumption. Ethanol utilization is on the rise in the United States, spurred by the biofuel utilization mandates put in place by the Energy Independence and Security Act of 2007 (EISA). The United States Environmental Protection Agency (EPA) has the statutory responsibility to implement the EISA mandates through the promulgation of the Renewable Fuel Standard. EPA may lower the biofuel consumption mandates in the event of insufficient supplies. At the time of enactment of EISA, gasoline blends in the United States were restricted by the

Clean Air Act to be less than 10% (E10) for use in non-flex-fuel vehicles. This 10% limit created a potential conflict between the two laws if gasoline consumption was not high enough to enable meeting the EISA consumption targets at a 10% or lower ethanol blend level. This conflict became known as the "blend wall." In response to this impending issue, the United States Department of Energy (DOE) undertook an ethanol mid-level blends testing program to investigate potential impacts on the legacy fleet that might result from increasing the allowable ethanol blend level from 10% to 15% or 20%. The largest effort in the program was a catalyst durability study that showed no significant increase

in catalyst degradation associated with aging vehicles using fuels containing 15% or 20% ethanol. Based on results of the DOE program, EPA granted partial approval to a waiver request for E15, allowing it in 2001 and newer vehicles, but denying its use in non-automotive engines such as lawn and garden equipment, snowmobiles, marine applications, etc [1,2]. As of this writing, a number of other required steps have yet to be taken that would make E15 legal for introduction into commerce.

EPA has historically mandated an emissions certification fuel specification that calls for ethanol-free fuel, except for the certification of flex-fuel vehicles. However, since the U.S. gasoline marketplace is now virtually saturated with E10, some organizations have suggested that inclusion of ethanol in emissions certification fuels would be appropriate. The test methodologies and calculations contained in the *Code of Federal Regulations* (CFR) for gasoline-fueled vehicles have been developed with the presumption that the certification fuel does not contain ethanol; thus, a number of technical issues would require resolution before such a change could be accomplished. This paper makes use of the considerable data gathered during the mid-level blends testing program to investigate one such issue: estimation of non-methane organic gas (NMOG) emissions. EPA has previously allowed manufacturers to estimate NMOG emissions as an alternative to conducting NMOG measurements for every emissions certification test [3]. This approach is not permitted for flex-fuel vehicles when fueled with ethanol, owing to the larger and more variable difference between NMHC and NMOG for these vehicles.

The definitions of regulatory hydrocarbon standards, including that of NMOG, are complex. In a typical emissions test, hydrocarbons are measured using a flame ionization detector (FID). The FID provides a measure of the hydrocarbons (HCs) in the sample through detection of ions produced when the HCs are burned in an ion-free hydrogen and oxygen flame. HC species have differing response factors in the FID, and hence this measurement is usually reported as parts-per-million equivalents of the calibration gas, usually a propane-in-air mixture. EPA terms this quantification of HCs as FIDHC [4]. This measurement is also commonly referred to as total hydrocarbons (THC), although the measurement does not account for the true total. Use of the term THC implies that the HC species have been quantified, then summed to achieve a "total" value. Although the FIDHC measurement has in one sense accomplished this measurement as it does not attempt to separate the species to begin with, no adjustments for the sensitivity of the FID to differing HC species have been made, and thus the term THC can be somewhat misleading. Many FID instruments are also equipped with a catalytic element that is used to eliminate all of the HCs other than methane (CH_4), allowing the instrument to have a CH_4 -only measurement capability. This capability allows a rapid determination of the CH_4 emissions following an emissions test. Use of a gas chromatograph

equipped with a flame ionization detector is also a commonly used method for relatively rapid characterization of the CH_4 portion of the FIDHC emissions. Both of these methods allow calculation of non-methane hydrocarbons (NMHC) by difference from FIDHC and CH_4 emissions measurements.

NMHC and NMOG emissions are often assumed to be virtually identical, but these two measures of HC emissions are not exactly the same. NMOG and NMHC are often of very similar magnitude, particularly when ethanol-free fuel is used. NMOG characterization begins with the basic measurement of NMHC as outlined above, but NMOG also includes the mass emissions of a number of oxygenated hydrocarbon species (OHC). These species are typically carbonyls and alcohols that can result from partial oxidation of fuel or from combustion of fuels that contain oxygen-bearing species such as ethanol. OHC measurements require the use of additional analytical tools and methods that are beyond the scope of this discussion other than to state that these techniques require a significant period of time to complete and are not typically available rapidly at the conclusion of an emissions test. As mentioned above, these measurements can be expensive and time consuming. Since the OHCs are generally small compared with NMHC for gasoline-fueled vehicles, EPA has traditionally allowed manufacturers to estimate the NMOG emissions by applying a multiplier of 1.04 to the NMHC mass emissions [3].

NMOG is not simply the arithmetic sum of the NMHC and OHC emissions. The response factors for FIDs to OHCs are variable depending upon the species but are generally less than unity. (Most non-oxygenated HC species exhibit response factors very close to unity.) The variability in response factors for OHCs is a result of the presence and location of oxygen atoms within the specific molecule. Since the FID has a positive fractional response to OHCs, a portion of the OHC mass emissions has already been measured as a part of FIDHC. It is necessary to account for this fraction during calculation of NMOG to avoid double-counting a portion of the HC mass. EPA provides for this accounting by subtracting fractions of the relevant OHC concentrations from the FIDHC concentration measurement and recalculating NMHC based on the corrected FIDHC concentration measurement. Unfortunately, this approach leads to the definition of NMHC being dependent upon whether or not NMOG speciation was performed [4]. This situation can result in confusion, and thus to resolve this issue the authors introduce the term non-oxygenated, non-methane hydrocarbons (NONMHC) to describe the HC emissions that are made up of FIDHC less the speciated methane and OHC mass emissions. In this way, NMOG is simply the arithmetic sum of NONMHC and OHC emissions, and both NMHC and NONMHC have consistent definitions regardless of whether OHC speciation is performed.

Regulatory standards for light-duty vehicle emission compliance in the United States are based on the use of the urban dynamometer driving schedule, typically referred to as

Table 1. Vehicle models included in the reported study.

Test Site	Model Year	Vehicle Model	Engine Family Number	Engine Displacement (Liters)	Engine Configuration	Emissions Standard
Southwest Research Institute, SwRI	2006	Chevrolet Silverado	6GMXT05.3379	5.3	V8	Tier 2 / Bin 8
	2007	Honda Accord	7HNXV02.4KKC	2.4	I4	Tier 2 / Bin 5
	2008	Nissan Altima	8NSXV02.5G5A	2.5	I4	Tier 2 / Bin 5
	2008	Ford Taurus	8FMXV03.5VEP	3.5	V6	Tier 2 / Bin 5
	2007	Chrysler Caravan	7CRXT03.8NEO	3.8	V6	Tier 2 / Bin 5
	2006	Chevrolet Cobalt	6GMXV02.4029	2.4	I4	Tier 2 / Bin 5
	2007	Dodge Caliber	7CRXB02.4MES	2.4	I4	Tier 2 / Bin 5
	2000	Chevrolet Silverado	YMXT05.3181	5.3	V8	Tier 1 / LDT 3
	2002	Nissan Frontier	2NSXT02.4C4B	2.4	I4	NLEV / LDT1
Transportation Research Center, TRC	2002	Dodge Durango	2CRXT04.75B0	4.7	V8	Tier 1 / LDT3
	2009	Jeep Liberty	9CRXT03.74PO	3.7	V6	Tier 2 / Bin 5
	2009	Ford Explorer	9FMXT04.03DC	4.0	V6	Tier 2 / Bin 4
	2009	Honda Civic	9HNXV01.8XB9	1.8	I4	Tier 2 / Bin 5
	2009	Toyota Corolla	9TYXV01.8BEA	1.8	I4	Tier 2 / Bin 5
	2005	Toyota Tundra	5TYXT04.0NEM	4.0	V6	Tier 2 / Bin 5
	2006	Chevrolet Impala	6GMXV03.9048	3.9	V6	Tier 2 / Bin 5
	2005	Ford F150	5FMXT05.4R17	5.4	V8	Tier 2 / Bin 8
	2006	Nissan Quest	6NSXT03.5G7B	3.5	V6	Tier 2 / Bin 5
	2003	Toyota Camry	3TYXV02.4HHA	2.4	I4	ULEV
	2003	Ford Taurus	3FMXV03.0VF3	3.0	V6	NLEV
	2003	Chevrolet Cavalier	3GMXV02.2025	2.2	I4	NLEV

the Federal Test Procedure, or FTP. The FTP consists of collecting a sample of the test vehicle's emissions during three phases, or bags. Bag 1, or the cold transient phase, is 505 seconds in length and is followed immediately by bag 2 (the cold-stabilized phase) without an engine shut-down. After bag 2 is completed, the vehicle is stopped and the engine turned off for a 10 minute soak. Bag 3 is conducted at the end of the 10 minute soak and is referred to as the hot-transient phase. The emissions results from FTP tests are a weighted combination of the mass emissions in all three of the driving phases and are typically referred to as the FTP weighted composite (or simply the composite) emissions result [4].

EXPERIMENTAL DATA

The data reported herein originated from mid-level ethanol blends tests that were conducted by Southwest Research Institute (SwRI) and Transportation Research Center, Inc. (TRC). The data reported in this paper were gathered from over 600 cold-start Federal Test Procedure (FTP) tests conducted on 68 vehicles representing 21 models from model years 2000 to 2009. Most of the vehicles were certified to the Tier-2 emissions standard, but several older Tier-1 and national low emissions vehicle program (NLEV) vehicles were also included in the study. Table 1 lists the vehicle models and their test location. The vehicles were acquired in matched sets of 3 or 4 units, and each vehicle of a set was dedicated to one fuel for aging and emissions testing. This approach helped eliminate unintended differences between vehicles that might impact the emissions data [5].

Emissions tests were conducted at three intervals between which the vehicles were driven a minimum of 25,000 miles (40,225 km). Lubricating oil changes were scheduled so that they did not occur less than 500 miles prior to an emissions test. Vehicles that were dedicated to ethanol-free fuel were only emissions tested on ethanol-free certification fuel, whereas vehicles using aging fuels that contained 10%, 15%, or 20% ethanol were emissions tested using a certification fuel that contained the appropriate ethanol content as well as an ethanol-free certification fuel. At least two replicate FTP tests were conducted for each vehicle, fuel, and mileage combination [5].

The emissions test fuels were splash-blends of ASTM D4806 fuel-grade denatured ethanol and emissions certification gasoline. TRC sourced these products from Chevron-Phillips Specialty Chemical Company. SwRI sourced their emissions fuel components from Haltermann Products. Three blend levels were used to conduct tests at TRC: ethanol-free (E0), 15% ethanol by volume (E15), and 20% ethanol by volume (E20). These same blend levels were also used for tests conducted at SwRI, but five vehicle sets at SwRI were also tested using a fuel containing 10% ethanol (E10). Multiple batches of each blend level were used at both test sites because of the scale and logistical limitations of the testing program. The blends contained the targeted ethanol content within about 1%, but the subsequent analysis of the ethanol content of each batch had a lower error level consistent with ASTM D4815 for the TRC fuels and ASTM D5599 for the SwRI fuels. Since the emissions fuels were splash-blends, the octane number, distillation, and other properties of the fuels varied according to the amount of ethanol in the blend [5].



Documents

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In all cases the exhaust from the vehicle was captured by a constant volume sampling system to enable proportional sampling during transient driving cycles. Proportional sampling is a technique for capturing a representative emissions sample during transient conditions in which the vehicle exhaust flow rate is changing. Constant volume sampling systems accommodate this transient exhaust flow by providing a varying dilution with fresh air so that the flow rate of the diluted exhaust is constant, thus enabling an accurate sample to be collected during the transient cycle. Ethanol emissions quantification was accomplished through the use of an impinger apparatus to trap the ethanol in the exhaust gas sample, followed by analysis using a gas chromatograph equipped with a flame ionization detector (GC/FID). Carbonyls were collected from the exhaust gas sample on dinitrophenylhydrazine (DNPH) cartridges, which were subsequently eluted and analyzed using high performance liquid chromatography (HPLC). Speciation measurements conducted during tests at SwRI were limited to ethanol, formaldehyde, and acetaldehyde. Data collected at TRC included a broader list of compounds, including those measured by SwRI and 13 additional carbonyl compounds. The remaining emissions constituents were measured using standard emissions instrumentation at both sites: photochemiluminescence instruments for NO_x and nondispersive infrared instruments for CO and CO_2 .

OHC SPECIATION RESULTS

The emissions test results from both sites showed that NMOG emissions for the FTP cycle were almost entirely produced in bag 1 (the cold transient phase), as expected. [Figure 1](#) shows the average fractionation of oxygenated species in bag 1 determined from the data collected at TRC. The total OHC mass emissions in bag 1 were typically less than 10 mg/mile for E0. OHC mass emissions were higher for E15 and E20, but were generally less than 50 mg/mile. The fractionation of OHCs from E0 tests shows that formaldehyde is the most prevalent individual species, followed by acetaldehyde and acetone. Formaldehyde alone accounts for about 35% of the OHCs from E0 operation, but the other species make up sizeable fractions of the OHCs as well. When ethanol is introduced into the fuel, however, the ethanol contribution dominates the overall OHC emissions, contributing over 75% of the total OHC mass emissions. Acetaldehyde becomes the second most prevalent species, with formaldehyde as a third. Acetone and acrolein become much less important contributors, and the remaining species individually have almost negligible impact on the OHC mass emissions. The fractions for the Tier-2 compliant vehicles are very similar to those of the non-Tier 2 vehicles, suggesting that the fractionation is not strongly a function of the emissions standard to which the vehicles were certified. Likewise, the species fractions for the E15 and E20 fuels are similar; suggesting that the presence of ethanol in the fuel is responsible for a large difference compared with ethanol-free

fuel, but the level of ethanol blended into the fuel may be of secondary importance. When the test fuel contains ethanol, the data indicates that three species (ethanol, acetaldehyde, and formaldehyde) make up 94% or more of the mass emissions of OHCs. Thus, measurements of these three species should be sufficient, in most cases, to characterize the NMOG mass emissions. Measurements of acetone and acrolein can provide a marginal impact on the measured NMOG mass, but even in bag 1 the average acetone plus acrolein emissions rate is only 0.66 mg/mile. The remaining compounds may be of special interest because of their health impacts in the environment but do not contribute significantly to NMOG mass emissions.

The relatively high fractional contributions of ethanol, formaldehyde, and acetaldehyde to overall OHC emissions make these three compounds the most important to characterize in order to provide an estimate of the overall NMOG emissions rate. The Tier-2 emissions regulations provide a regulatory standard of 0.018 g/mile for formaldehyde but do not provide a standard for acetaldehyde, though this compound was included in EPA's previous list of mobile-source air toxic compounds [6]. The relative proportions of the individual OHC species in general agree with a recent speciation study conducted at the Massachusetts Institute of Technology (MIT), with the exception that the MIT study did not report formaldehyde emissions [7].

The increase in the ethanol emissions fraction is of course due to an increase in the emissions of this compound associated with its inclusion in the fuel. Tests conducted with E0 fuel exhibited very nearly zero ethanol emissions. Formaldehyde is present at low levels in the exhaust even for tests conducted with E0. [Figure 2](#) shows the bag 1 emissions rate of formaldehyde compared with overall bag 1 NMOG emissions. In general, the formaldehyde emissions from ethanol-blended fuels are on the same order as for ethanol-free fuel, though there is an inconsequential, but statistically significant, increase in formaldehyde associated with ethanol-blended fuels [5]. Thus, the decrease in the formaldehyde fraction of total OHCs is due mostly to the increase of other species such as ethanol, not due to large decreases in formaldehyde emissions. As expected, acetaldehyde emissions increased when ethanol was present in the fuel. The bag 1 acetaldehyde emissions are shown in [Figure 3](#) as a function of the bag 1 NMOG emissions. It is worthy of note that although the OHC emissions increase when ethanol is added to the fuel, the overall OHC emissions levels remain very low on a mass basis. A breakdown of the bag 1 OHC mass emissions is shown in [Figure 4](#). The OHC mass emissions approach zero for E0 fuels and increase with ethanol content. No regulatory limit exists for bag 1 alone; however, if bags 2 and 3 have zero emissions, the weighted composite emissions result is approximately 20% of the bag 1 rate. Thus, multiplying the appropriate statutory limit by a factor of five is useful in examining the magnitude of bag 1 results. The statutory limit for formaldehyde under Tier 2 regulations is 0.018 g/mile for Bins 5-8, hence, the y-axis