

A Complete Assessment of the Emissions Performance of Ethanol Blends and Iso-Butanol Blends from a Fleet of Nine PFI and GDI Vehicles

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ABSTRACT

Biofuels, such as ethanol and butanol, have been the subject of significant political and scientific attention, owing to concerns about climate change, global energy security, and the decline of world oil resources that is aggravated by the continuous increase in the demand for fossil fuels. This study evaluated the potential emissions impacts of different alcohol blends on a fleet of modern gasoline vehicles. Testing was conducted on a fleet of nine vehicles with different combinations of ten fuel blends over the Federal Test Procedure and Unified Cycle. The vehicles ranged in model year from 2007-2014 and included four vehicles with port fuel injection (PFI) fueling and five vehicles with direct injection (DI) fueling. The ten fuel blends included ethanol blends at concentrations of 10%, 15%, 20%, 51%, and 83% by volume and iso-butanol blends at concentrations of 16%, 24%, 32%, and 55% by volume, and an alcohol mixture giving 10% ethanol and 8% iso-butanol in the final blend.

The results showed some clear trends with increasing levels of alcohol in the blends for some pollutants, but not for others. There was a trend for lower CO, CO₂, PM mass, and particle number, and lower fuel economy with higher alcohol content fuels. For other pollutants, such as THC, NMHC, CH₄, and NO_x, there were not strong fuel trends, while some carbonyl species showed some trends towards higher emissions for higher alcohol blends. The emissions profiles for the different vehicles also showed differences, with the wall-guided DI vehicles showing higher PM mass, and particle number compared to the PFI vehicles.

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INTRODUCTION

Ethanol use in liquid transportation fuels has grown significantly in recent years. Use of ethanol as a transportation fuel in the United States (US) increased approximately 6-fold over the period 2002-2012, from 2 to 13 billion gallons per year [1]. The trend of increasing ethanol use in the US, Europe, and elsewhere is driven by the desire to decrease petroleum usage and imports, reduce emissions from older vehicles, provide economic development in the agricultural sector, and reduce emissions of greenhouse gases (GHGs). In the US alone, the increased use of ethanol in the coming years will also be a result of the Renewable Fuel Standard (RFS) Program Final Rule, which mandates the use of 36 billion gallons of renewable fuels to be blended into transportation fuel by 2022, with ethanol expected to make up the majority of this requirement. The European Union (EU) has also adopted a proposal for a directive on the promotion of the use of biofuels with targets of 5.75% by 2010 and 10% by 2020 [2]. Although biodiesel has been the biofuel of choice in Europe, ethanol has also gained an important market share in various European countries, reaching a total EU production of 2.8 million tons of oil equivalent (toe) in 2010 [3].

In many parts of the US, ethanol is currently blended into gasoline at a concentration of 10% by volume (E10). Ethanol is also available as E85, which after a recent change in specifications, is allowed to contain as much as 83% v/v and as little as 51% v/v ethanol. Vehicles designed to use higher blends of ethanol are known as flexible fuel vehicles (FFVs). FFVs have historically been designed for operation on E0/E10 and E85 and are certified for emissions compliance by testing with E0 and E85. Addition of ethanol to gasoline comes with some challenges, since ethanol has rather different physical and chemical characteristics than gasoline, which could potentially affect the performance and efficiency of spark-ignition (SI) engines. Adding ethanol into gasoline potentially increases the Reid vapor pressure (RVP) of the blend and alters the distillation properties [4, 5]. Ethanol is highly water soluble, making it incompatible with the existing infrastructure and pipeline transportation processes due to the risk of water-induced phase separation [6]. The net heating value of ethanol is also about one-third less than gasoline on a volumetric basis. While this difference reduces the volumetric fuel economy (miles per gallon), ethanol can provide a small improvement in the thermal efficiency of engine operation (miles per gallon of gasoline-equivalent) [7].

The drawbacks that have been identified with ethanol use have led to research into the use of higher molecular weight alcohols as gasoline extenders. Currently, an alternative bio-alcohol for use in SI engines without modification is butanol [8, 9]. Butanol is a four carbon alcohol compound, which exists as four different chemical isomers depending on the location of hydroxyl group ($-OH$) and the carbon bond structure. This emphasis on butanol has also been reflected on a regulatory level, with ASTM D7862 announced for blends of butanol with gasoline of 1 to 12.5% by volume in automotive SI engines. The specification covers three butanol isomers including 1-butanol, 2-butanol, and 2-methyl-1-propanol (iso-butanol). The specification specifically excludes 2-methyl-2-propanol (tert-butanol), because it has different physical properties (melting point, water miscibility) than the other three butanol isomers. Butanol offers a number of advantages over ethanol for transportation use. Butanol is less corrosive than ethanol, has a higher energy content than ethanol, and more closely resembles gasoline in physical properties [10]. In comparison to ethanol, butanol has a higher tolerance to water contamination, potentially allowing its use in existing distribution pipelines. Butanol also has a lower volatility than ethanol and thus a lower tendency towards cavitation and vapor lock problem [11, 12].

In addition to the mandates to introduce higher levels of alternative fuels into the fuel pool, more stringent carbon dioxide (CO_2) emissions limits have also been put in place for automotive manufacturers. This has led to efforts by the automotive manufacturers to try to improve the overall efficiency of gasoline powered passenger cars. To reach these new CO_2 targets, different strategies have been studied, including engine downsizing and higher boost pressures in combination with direct gasoline injection. Spark ignition direct injection (SIDI) engines can offer up to a 25% improvement in fuel economy compared with port fuel injection (PFI) SI engines [13]. However, SIDI engines produce higher particulate matter (PM) emissions compared to PFI engines [14, 15], and compared with modern diesel engines equipped with diesel particle filters (DPFs) [16, 17]. For SIDI engines, there can be issues relating to fuel preparation, including fuel contact with the cylinder wall surfaces during combustion, which leads to the formation of soot because the wall quenches the flame and prevents complete combustion of the fuel, especially during the cold-start [18]. Currently, most SIDI engines employ wall-guided designs, in which the fuel spray is directed from a side-mounted fuel injector towards a contoured piston and then upward toward the spark plug [13]. Alternative designs to wall-guided SIDI engines use either homogeneous or stratified-charge spray-guided configurations [19]. For the spray-guided SIDI configuration, the fuel injector and spark plug electrodes are close-spaced in the center of the chamber. The fuel injector confines the fuel spray such that it does not contact the cylinder walls, thus reducing the incidence of fuel wall wetting, improving mixing and reducing soot formation [19, 20].

The use of ethanol blends has been widely investigated in PFI engines and vehicles, and in older technology vehicles, while there are fewer studies available on the effects of ethanol blends from modern technology SIDI engines and vehicles. Karavalakis et al. [21] found that total hydrocarbon (THC), non-methane hydrocarbon (NMHC), and carbon monoxide (CO) emissions were lower with ethanol blends for PFI vehicles, while nitrogen oxide (NO_x)

emissions showed some increases with increasing ethanol content in gasoline. These trends were more consistent for the older SI-PFI vehicles in the study. They also found higher acetaldehyde and some higher formaldehyde emissions with the ethanol blends, whereas the toxic compounds of benzene and 1,3-butadiene were lower. Bielaczyc et al. [22] showed small reductions in THC, CO, and NO_x emissions from SI-PFI vehicles with higher ethanol blends over the New European Driving Cycle (NEDC). They also found that the addition of ethanol caused a decrease in the number of particles and a significant reduction in PM mass emissions. Hubbard et al. [23] reported increases in acetaldehyde, formaldehyde, methane (CH_4), and ammonia with increasing ethanol content in the fuel when they tested a 2006 model year FFV over the Federal Test Procedure (FTP) cycle. They also found lower NO_x and NMHC emissions compared to E0. Similar findings were seen by Yanowitz and co-workers [24] when they tested nine FFVs over the LA92 test procedure. They found reductions in NO_x , CO, and CO_2 , as well as increases in emissions of ethanol, acetaldehyde, and formaldehyde with increasing ethanol concentration. Recently, Mamakos and colleagues found large reductions in particle number and PM mass emissions from a Euro 5 SIDI-FFV with the use of 75-85% ethanol/gasoline blends over the NEDC and the Artemis cycles [25]. Magara-Gomez and co-workers [26] also showed reductions in particle number emissions with E85 and E65 compared to E35 and E6 when they tested a 2007 model year PFI-FFV over the LA92 cycle. Storey et al. [27] analyzed the effect of E10 and E20 blends on a 2007 model year SIDI vehicle and found that NO_x , CO, formaldehyde, and benzaldehyde emissions decreased with higher ethanol blends, while acetaldehyde emissions showed increases. They also showed reduced PM mass and particle number emissions with ethanol blends. Maricq et al. [28] showed small reductions in PM mass and particle number emissions as the ethanol level in gasoline increased from 0 to 20% when they tested a SIDI turbocharged vehicle with two engine calibrations over the FTP.

Butanol has not been studied as extensively as ethanol in modern technology engines/vehicles. Dernote et al. [29] assessed different n-butanol-gasoline blends at different engine loads, spark timings, and equivalence ratios in a SI-PFI engine. They found some THC reductions with butanol, while no significant differences were seen in NO_x emissions. It was also found that adding butanol improved combustion stability. Schulz and Clark [30] carried out a study comparing various ethanol blends and a 16% n-butanol blend using six modern technology vehicles over the FTP cycle. They found a limited number of statistically significant differences between the fuels tested, however, a decreasing trend in CO and formaldehyde emissions was observed with the butanol blend compared to gasoline. Stansfield et al. [31] tested an unmodified 2009 SIDI vehicle over the NEDC on various ethanol and iso-butanol blends. They found that Bu16 and Bu68 blends showed lower THC and CO emissions than the gasoline fuels, while NO_x emissions were unaffected. PM mass emissions for Bu16 were lower compared to gasoline fuels, while Bu68 showed significant increases. Storey et al. [32] compared the emissions from a iBu48 blend to E30 and E0 for a SIDI engine. They found PM mass was similar for the E0 and Bu48 blends, but lower for the E30, while particle number emissions for Bu48 fell between those for E0 and E30. They also found the Bu48 produced higher emissions of C4 aldehydes. Similar results were seen by Ruffing et al. [33] when they tested a SIDI turbocharged vehicle with two engine calibrations over the FTP.

[33] when they tested a 2009 PFI vehicle on gasoline, E16, nBu17, iBu21, and a mixture of iBu12E7. The authors also found an increase in formaldehyde emissions from iso-butanol blend compared to gasoline. Wallner and Frazee [34] found that NO_x , CO, and THC emissions were lower with increasing n-butanol and iso-butanol contents in gasoline, while some increases were seen for formaldehyde and acetaldehyde emissions when they utilized n-butanol and iso-butanol as blending agents with gasoline in SIDI engine. In a similar study, the same authors showed lower volumetric fuel consumption and lower NO_x emissions for both n-butanol and iso-butanol isomers compared to ethanol blends [35].

This study was designed to examine the effects of low-, mid-, and high-level ethanol and iso-butanol blends on criteria emissions, gaseous toxic pollutants, and particulate emissions from a fleet of nine light-duty vehicles with different injection strategies. The study utilized a total of ten alcohol blends, including 10%, 15%, 20%, 51%, and 83% ethanol blends and 16%, 24%, 32%, and 55% iso-butanol blends, and an alcohol mixture giving 10% ethanol and 8% butanol in the final blend. Testing was conducting over the FTP and the Unified Cycle (UC) that included effects of both cold-start and transient operation. A major goal of this study was to investigate the influence of fuel type, engine technology, and driving conditions on gaseous and particulate emissions.

EXPERIMENTAL

Test Fuels and Vehicles

A total of ten fuels were employed in this study. The fuel test matrix included an E10 fuel (10% ethanol and 90% gasoline), which served as the baseline fuel for this study, and four more ethanol blends, namely E15, E20, E51, and E83. The ethanol fuels were blended by Haltermann Solutions, Channelview, TX to represent ethanol fuels that would be utilized in California, in terms of properties such as aromatic content, Reid Vapor Pressure (RVP), and other properties. The two highest ethanol blends represent the upper and lower blend limits of the current E85 specification.

For this study, iso-butanol was blended with gasoline at proportions of 16% (Bu16), 24% (Bu24), 32% (Bu32), and 55% (Bu55) by volume. The blends of Bu16, Bu24, and Bu32 are the equivalents of E10, E15, and E20, respectively, based on the oxygen content. In addition, an alcohol mixture giving 10% ethanol and 8% iso-butanol in the final blend (E10/Bu8) was used. This mixed alcohol formulation was equivalent to E15 based on the oxygen content. Most fuels were custom blended to match the oxygen contents, maintain RVP within certain limits (42.4-49.64 kPa), and match the fuel volatility properties, except the E10/Bu8 fuel that was a 50/50 splash blend of the E20 and Bu16 fuels. For the Bu55 blend, this was the highest volume of iso-butanol that could be blended while still maintaining acceptable driveability characteristics, as determined by the driveability index and fuel volatility. The main physicochemical properties of the ethanol and butanol test fuels are presented in [Table A1](#) and [Table A2](#), respectively (see [Appendix](#)).

Testing was conducted on nine light-duty gasoline vehicles of different designs (passenger cars and trucks). The vehicles included a 2007 model year (MY) Honda Civic, a 2007 MY Dodge Ram, a 2012 MY Toyota Camry, a 2012 MY Kia Optima, a 2012 MY Chevrolet Impala, a 2012 MY Mazda3, a 2012 MY Mercedes Benz, a 2013 MY Ford F-150 FFV, and a 2014 MY Chevrolet Silverado FFV. All vehicles were operated stoichiometrically and were equipped with three-way catalysts (TWC). The 2007 Honda Civic, 2007 Dodge Ram, 2012 Toyota Camry, and 2013 Ford F-150 vehicles were all equipped with SI-PFI engines, whereas the other test vehicles were equipped with SIDI engines. For the SIDI engines, the 2012 Kia Optima, 2012 Chevrolet Impala, 2012 Mazda3, and 2014 Chevrolet Silverado utilized wall-guided designs, while the 2012 Mercedes Benz utilized a spray-guided design. The Honda Civic, Dodge Ram, Toyota Camry, Kia Optima, Chevrolet Impala, Mazda3, Mercedes Benz, Ford F-150, and Chevrolet Silverado had 29,000 miles, 52400 miles, 13,500, 11,824, 25,372, 18,851, 10,996, 13,687, and 2,649 miles, respectively, at the start of the test campaign. The main technical specifications of the test engines are provided in [Table A3](#) (see [Appendix](#)).

The Honda Civic was certified to the US Tier 2 Bin 5/California Low Emission Vehicle (LEV) II, Ultra Low Emission Vehicle (ULEV) emissions standards, the Dodge Ram was certified to the US Tier 2 Bin 4/LEV II emissions standards, the Toyota Camry met the US Tier 2 Bin 5/PZEV emissions standards, the Kia Optima was certified to the Federal Tier 2, Bin 2 emission standard, the Chevrolet Impala, Mazda3, and Mercedes Benz, were certified to the California LEV II, Super ultra-low emission vehicle (SULEV) emission standard, and the Ford F-150 and Chevrolet Silverado were certified to the California LEV II, ULEV emission standard. It should be noted that not every vehicle was tested on all fuels. Only the Toyota Camry and the Kia Optima were tested on the E10/Bu8 mixture. The higher ethanol (E55 and E83) blends and the iso-butanol (Bu55) blend were only tested on the FFVs, namely the Ford F-150 and the Chevrolet Silverado.

Driving Cycles and Measurement Protocol

Three FTP and three UC tests were conducted on each fuel tested on each test vehicle. The six tests on a particular fuel were conducted sequentially once the vehicle was changed to operate on that fuel, and the fuel was not changed to another fuel during this time.

Prior to testing any particular vehicle, an extensive preconditioning procedure was followed regarding oil and fuel changes. [Figure A1](#) ([Appendix A](#)) summarizes the oil pre-conditioning and fuel change procedures in a flow chart. Prior to beginning testing on a vehicle, its lubricant oil was changed. Following the oil change, the vehicle was conditioned on the oil over two US06 cycles, followed by an LA4 and a US06 cycle sequence repeated twice (i.e., a total of 4 US06 cycles and 2 LA4s). The vehicle fuel preconditioning procedure incorporated multiple fuel drains and fills to ensure complete changeover of the fuel and to minimize or eliminate carryover effects between test fuels. The preconditioning procedure was similar to that specified in the Code of Federal Regulations (40 CFR 86.132-96). This drain and fill sequence included two drain and 209 mm and a drain and 3 gallon fill. After the drain and 3 gallon fill, and the first

drain and 40% fill, the vehicle was then conditioned either on the road or on the dynamometer over the Urban Dynamometer Driving Schedule (UDDS)/LA4, or the first two bags of the FTP. The on-road course was designed to simulate the LA4 portion of the FTP in terms of typical speeds as well as number of stops. In between drain and fill and preconditioning cycles, the vehicle was idled one or two times for two minutes with the vehicle being rocked back and forth. Following the first LA4, a sequence of engine off and idles was performed along with a drain and 40% fill. After this sequence, the vehicle was given its final preconditioning LA4 on the dynamometer, and then placed into cold soak overnight prior to performing the FTP or UC test.

Emissions Testing and Analysis

All tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL), which is equipped with a Burke E. Porter 48-inch single-roll electric dynamometer. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system was used to obtain certification-quality emissions measurements. For all tests, standard bag measurements were obtained for THC, CO, NO_x, NMHC, and CO₂. NMHC was determined from the combined results from the THC analyzer and a separate CH₄ analyzer. Bag measurements were made with a Pierburg AMA-4000 bench.

Samples for carbonyl analysis were collected cumulatively over the entire FTP on 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA). Sampled cartridges were extracted using 5 mL of acetonitrile and injected into an Agilent 1200 series high performance liquid chromatograph (HPLC) equipped with a variable wavelength detector. The column used was a 5 µm Deltabond AK resolution (200cm × 4.6mm ID). The HPLC sample injection and operating conditions were set up according to the specifications of the SAE 930142HP protocol.

Samples for 1,3-butadiene, benzene, toluene, ethylbenzene, and xylenes were collected using Carbotrap adsorption tubes consisting of multi-beds, including a molecular sieve, activated charcoal, and carbotrap resin. An Agilent 6890 GC with a flame ionization detector (FID) maintained at 300 °C was used to measure volatile organic compounds. A Gerstel TDS thermal adsorption unit was used for sample injection. This unit ramps the temperature from 30 °C to 380 °C at a rate of 6 °C per minute to desorb the sample from the tubes. A 60 m × 0.32 mm HP-1 column was used. For these analyses, the GC column and operating conditions were set up according to the specifications of SAE 930142HP Method-2 for C₄-C₁₂ hydrocarbons. It should be noted that the amount of sample that is collected and injected into the GC using the Carbotrap absorption tubes is considerably greater than what can be achieved using Tedlar bag samples, since the absorption tubes are sampled over the duration of the test cycle, and hence allow for much larger equivalent volume of sample to be injected into the GC. Thus, the detection limits with the thermal desorption tubes are improved by several orders of magnitude compared to levels achieved in earlier Auto/Oil programs.

PM measurements were made on both a mass and number basis. PM mass samples were collected cumulatively over the entire FTP and UC cycles, with one sample collected for each test. Total PM mass determinations were collected using 47 mm Teflon® filters and measured with a 1065-compliant microbalance in a temperature and humidity controlled clean chamber. Particle number measurements were made with a TSI model 3772 condensation particle counter (CPC) for the Honda Civic and Dodge Ram and a TSI model 3776 CPC for the Toyota Camry, Kia Optima, Chevrolet Impala, Mazda3, Mercedes Benz, Ford F-150, and Chevrolet Silverado. The TSI 3772 was replaced by the TSI 3776, since the 3776 CPC has a lower cut point, 2.5 nm compared to 10 nm for the TSI 3722, and also provides a real-time coincidence correction up to 300,000 particles per cm³. An ejector diluter was used to collect samples from the CVS tunnel.

Statistical Analysis

Statistical analyses for each pollutant were run using the Mixed procedure in PC/SAS from SAS Institute, Inc. The mixed models were performed for each pollutant to determine the statistical significance of any fuels effects. The fuel type and the test type (i.e., FTP or UC) were included in the models as fixed effects, the vehicle was a random effect. The statistical analyses were run separately for the seven non-FFVs and the two FFVs, because they were tested on a different set of fuels.

Analyses were run using the logarithmic transform of the data, as previous studies have shown that the emissions standard deviation is relatively constant as a percentage of the emission level. For example, vehicles with higher emission levels will tend to have a higher variability on an absolute basis than those with lower emissions levels. Examination of the current data revealed that this relationship between the emissions level and variability held true even for the very low emitting vehicles. The normality of residuals was checked in the models for all regulated and toxic emissions to determine if a transformation was necessary. The fuel economy was analyzed in the inverse scale (i.e., gallons/mile). For emissions components that included zeros for individual bags or weighted emissions, a small constant was added prior to taking the logarithm to allow the analyses to be done in the logarithm scale. Any added constants were selected to be as small as possible, and in all cases did not exceed the background levels.

ANOVA results were considered to be statistically significant for $p \leq 0.05$ and marginally statistically significant for cases where $0.05 < p \leq 0.1$. Pairwise comparisons were made using a least squares means test. The results from the logarithmic or inverse models were "back transformed" to provide least square means for all pollutants on each fuel. This provides an arithmetic measure to evaluate the magnitude of any statistically significant effects. Any constants added to facilitate the analysis in logarithm scale were subsequently subtracted from the least square means once the back transformation to the arithmetic scale was made.

RESULTS AND DISCUSSION

The figures for each emissions component show the results for each vehicle/fuel/cycle combination based on the average of the tests conducted on that particular test combination. The error bars on the figures are the standard deviation over all tests for each test combination. Note that since the statistical analyses were run with test type as a fixed effect, the percent differences provided in the text represent percentage differences based on the combined results of the FTP and UC testing, unless the ANOVA showed that there was a statistically significant fuel-test cycle interaction. In the cases where a statistically significant fuel-test cycle interaction was found, indicating that the fuel effects were different for the two cycles at a statistically significant level, the least square means (LSMs) were determined separately and reported separately for the FTP and the UC. In addition to the fleetwide statistical analysis results, in a limited number of cases, additional fuel trends for individual vehicles are also discussed where the comparisons are noteworthy.

THC, NMHC, and CH₄ Emissions

THC emissions for all vehicle/fuel combinations over the FTP and UC test cycles are shown in Figure 1 (a, b). In general, THC emissions were found at low levels for all nine vehicles for both test cycles, ranging from 0.005 to 0.124 g/mile for the FTP and 0.005 to 0.093 g/mile for the UC. Higher THC emissions were observed for the older model PFI fueled Honda Civic and Dodge Ram vehicles and both FFVs compared to the other vehicles. Overall, the largest portion of THC emissions was emitted during the first 200-300 seconds of the FTP and UC cycles (bag 1) when the engine was cold. Cold-start THC emissions over the FTP and UC tests cycles, respectively, ranged from 0.098-0.140 g/mile and 0.281-0.335 g/mile for the Honda Civic, 0.227-0.675 g/mile and 0.536-1.135 g/mile for the Dodge Ram, 0.014-0.028 g/mile and 0.043-0.102 g/mile for the Toyota Camry, 0.026-0.068 g/mile and 0.072-0.394 g/mile for the Kia Optima, 0.020-0.059 g/mile and 0.061-0.106 g/mile for the Chevrolet Impala, 0.030-0.064 g/mile and 0.087-0.225 g/mile for the Mercedes Benz, 0.025-0.039 g/mile and 0.080-0.143 g/mile for the Mazda 3, 0.115-0.213 g/mile and 0.156-0.497 g/mile for the Ford F-150, and 0.091-0.252 g/mile and 0.236-0.786 g/mile for the Chevrolet Silverado. The higher cold-start THC emissions can be attributed to incomplete combustion products from the fuel enrichment during start up and from the reduced catalyst efficiency, as the catalyst is below its light-off temperature during a good portion of the cold-start phase. The cold start emissions for the UC are higher than those for the FTP because bag 1 for the UC cycle is shorter, and hence the fraction of time when the catalyst is below its light-off temperature is greater for the UC bag 1. THC emissions for the hot-running and hot-start phases were practically eliminated, as the TWC was highly efficient in oxidizing the hydrocarbon fuel fractions once it had reached its light-off temperature. Higher cylinder surface temperatures during the hot-running and hot-start phases would also aid in better fuel vaporization and avoiding pool fires.

There were no consistent fuel effects for the weighted THC emissions over the conventional vehicle fleet or for the FFVs. For the non-FFVs, cold-start THC emissions showed statistically significant differences between fuels, but not for the two FFVs. For the non-

FFVs, cold-start THC emissions showed a marginally statistically significant increase of 16% ($p=0.0539$) for E15 compared to E10, while the alcohol mixture E10/Bu8 showed statistically significant reductions of 28% ($p=0.0008$), 23% ($p=0.0218$), 23% ($p=0.0232$), 27% ($p=0.0026$), and 25% ($p=0.0087$), respectively, compared to the E15, E20, Bu16, Bu24, and Bu32 blends over the combined FTP and UC cycles. For both the non-FFVs and FFVs, there were no statistically significant differences between fuels for the hot-running emissions of the FTP or UC cycle. For the hot-start THC emissions, the non-FFVs did not show any strong fuel effects for either of the test cycles. For the FFVs, the only statistically significant effect in hot-start THC emissions was a 38% ($p=0.0064$) reduction for Bu55 relative to E83.

In comparison with previous studies, trends of decreasing THC emissions with increasing alcohol concentration have generally been seen for test cell engines or larger fleets of older technology vehicles [21,29,36, 37]. This phenomenon has been widely attributed to the presence of oxygen content in the fuel, which leans the air-fuel ratio and promotes oxidation during combustion and over the catalyst. On the other hand, some increases in THC emissions with ethanol and butanol fuels have been observed in previous studies conducted with test cell engines and light-duty vehicles [28,38]. The lack of consistent fuel trends for THC emissions for the conventional vehicles and FFVs in the present study suggests THC emissions from modern vehicles with more sophisticated engine controls and catalysts are not as significantly impacted by the oxygen content of the fuel. For the SIDI vehicles, higher THC emissions were likely because of fuel impingement on combustion chamber surfaces. It is therefore reasonable to assume that a portion of THC emissions might be derived from unburned fuel during the initial stages of the cold-start portions of the FTP and UC.

NMHC emissions are shown in Figure 2 (a, b). NMHC emissions followed similar patterns with THC emissions for most vehicles over both cycles. Analogous to THC emissions, the cold-start phase dominated the NMHC emissions, with the hot-running (bag 2) and hot-start (bag 3) NMHC emissions being at very low concentrations for most vehicles compared to bag 1 emission levels. Statistical analysis showed that for the conventional non-FFVs, the weighted NMHC emissions did not show any significant fuel effects, while for the FFVs the weighted NMHC emissions showed some statistically significant differences. For the FFVs, the weighted NMHC emissions showed a statistically significant decrease of 29% for E83 compared to the baseline E10 blend. For the cold-start phase, NMHC emissions did not show any fuel effects for the FFVs, but showed strong differences between fuels for the conventional non-FFVs. Similar to cold-start THC emissions, cold-start NMHC emissions showed a marginally statistically significant increase of 17% ($p=0.0503$) for E15 relative to E10, while the mixture E10/Bu8 showed statistically significant decreases of 28% ($p=0.0016$), 22% ($p=0.0438$), 23% ($p=0.0344$), 27% ($p=0.0053$), and 24% ($p=0.0238$), compared to the E15, E20, Bu16, Bu24, and Bu32 blends. For both the non-FFVs and FFVs, there were no consistent fuel effects for the hot-running and hot-start NMHC emissions for the FTP and UC cycles.

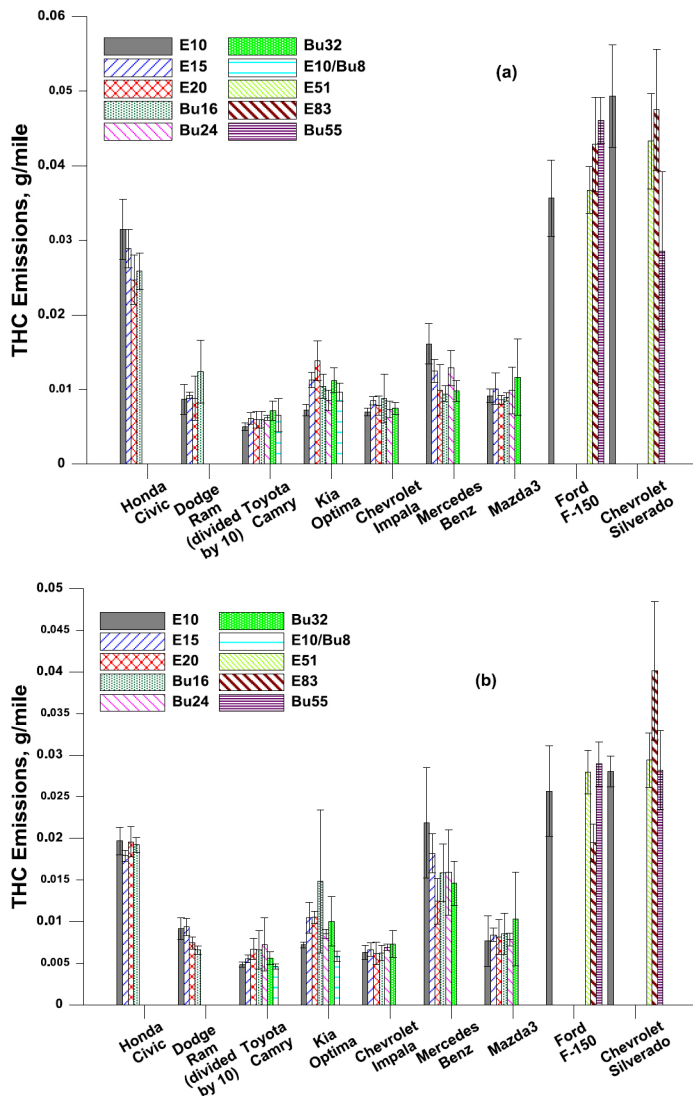


Figure 1. (a-b). THC emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent $\pm$ one standard deviation around the average value for each fuel.

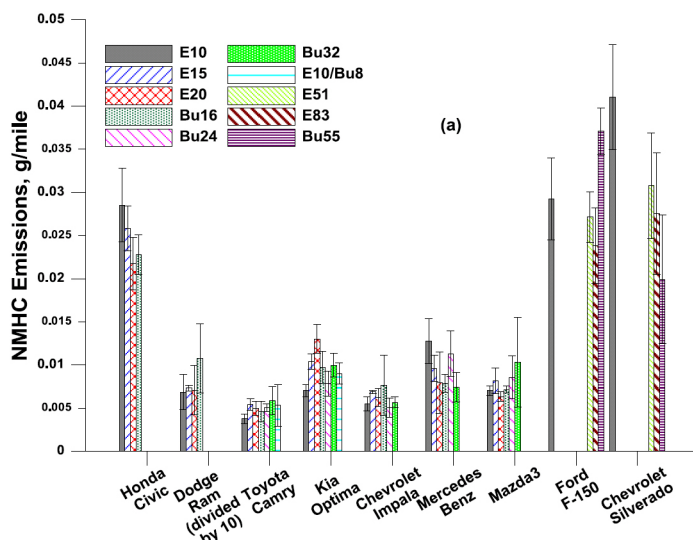


Figure 2. (a-b).

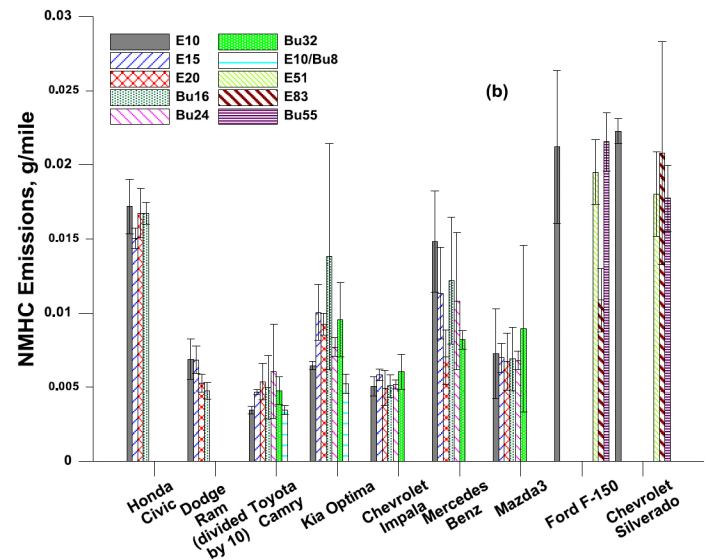


Figure 2. (a-b). (cont.) NMHC emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent $\pm$ one standard deviation around the average value for each fuel.

Although the emissions of CH_4 can contribute significantly to total CO_2 -equivalent GHG emissions, CH_4 emissions from mobile sources are not regulated in the US, as opposed to the EU. CH_4 is a more potent GHG compared to CO_2 , with a potency 21 times greater than CO_2 over 100 years, but CH_4 emissions are generally very low compared to CO_2 emissions. Emissions of CH_4 are a function of the type of fuel used, the design and tuning of the engine, the type of emission control system, the age of the vehicle, as well as other factors. As shown in Figure 3(a, b), CH_4 emissions were found at very low levels ranged from 0.001 to 0.023 g/mile for the FTP and from 0.001 to 0.026 g/mile for the UC.

CH_4 emissions did not show any statistically significant differences between fuels for the weighted emissions of the FTP or UC cycle for the non-FFV vehicles. For the FFVs, however, weighted CH_4 emissions showed strong fuel differences for the FTP and UC cycles. For the FFVs, weighted CH_4 emissions showed statistically significant increases of 74% ($p \leq 0.0001$), 163% ($p \leq 0.0001$), and 43% ($p = 0.0002$), respectively, for E51, E83, and Bu55 compared to E10. A statistically significant increase in weighted CH_4 emissions of 51% ($p \leq 0.0001$) was also seen for E83 compared to E51, and a marginally statistically significant reduction of 17% ($p = 0.0806$) for Bu55 compared to E51.

For the cold-start CH_4 emissions, the non-FFVs showed statistically significant reductions for the alcohol mixture E10/Bu8 of 27% ($p = 0.0074$), 27% ($p = 0.0083$), 27% ($p = 0.0117$), and 31% ($p = 0.0011$), respectively, compared to E15, E20, Bu24, and Bu32 blends, while a marginally statistically significant decrease of 22% ($p = 0.0860$) was seen for the E10/Bu8 alcohol mixture compared to Bu16. For the FFVs, cold-start CH_4 emissions showed statistically significant increases of 66% ($p \leq 0.0001$), 172% ($p \leq 0.0001$), and 40% ($p = 0.0029$), respectively, for E51, E83, and Bu55 compared to E10. In addition, E83 showed a statistically significant increase of 64% ($p \leq 0.0001$) compared to E51 and Bu55 showed a statistically significant reduction of 49% ($p \leq 0.0001$) compared to E83. For the

conventional non-FFVs, CH₄ emissions did not show any statistically significant differences between fuels for the hot-running and hot-start phases of the FTP or the UC cycles. For the FFVs, on the other hand, the fuel and driving cycle effects were particularly strong on the hot-running CH₄ emissions. For the hot-running FTP CH₄ emissions, E83 showed a statistically significant increase of 106% ($p=0.0190$) and a marginally statistically significant increase of 71% ($p=0.0904$), respectively, compared to the E10 and E51 blends, whereas Bu55 showed a statistically significant decrease of 57% ($p=0.0072$) relative to E83. For the hot-running UC CH₄ emissions, E51, E83, and Bu55 showed sharp increases of 268% ($p=0.0031$), 273% ($p=0.0028$), and 262% ($p=0.0035$), respectively, compared to the baseline E10, at a statistically significant level. For hot-start CH₄ emissions, fuels E51 and E83 showed statistically significant increases of 42% ($p=0.0007$) and 111% ($p\leq 0.0001$), respectively, compared to E10. For the hot-start CH₄ emissions, E83 showed an increase of 48% ($p=0.0001$), compared to E51, and Bu55 showed a decrease of 27% ($p=0.0021$) and 51% ($p\leq 0.0001$), respectively, compared to E51 and E83, all at a statistically significant level.

In general, it is expected that the use of alcohol fuels will decrease the emissions of CH₄ from SI combustion. The precursors of CH₄ formation are CH₃ and C₈H₁₈, which suggests that the addition of either ethanol or butanol to gasoline will inhibit the production of CH₄ via the C₈H₁₈ decomposition pathway [39]. Under the present test conditions, our results did not reveal a global trend of lower CH₄ emissions with alcohol fuel formulations for the non-FFVs, but for the FFVs substantial increases in CH₄ emissions with E51, E83, and Bu55 compared to E10 were found. Cold-start CH₄ emissions were found to be somewhat higher compared to hot-running and hot-start phases for both cycles. The differences in CH₄ emissions between the cold and warm phases of the FTP and UC tests were not as pronounced as those found for THC and NMHC. This was probably due to the fact that CH₄ is a more inert gas in terms of its oxidation activity in the TWC. So, the reductions in CH₄ emissions during the hot-running and hot-start phases due to activation and light-off of the TWC are not as significant as the corresponding reductions seen for the THC and NMHC emissions.

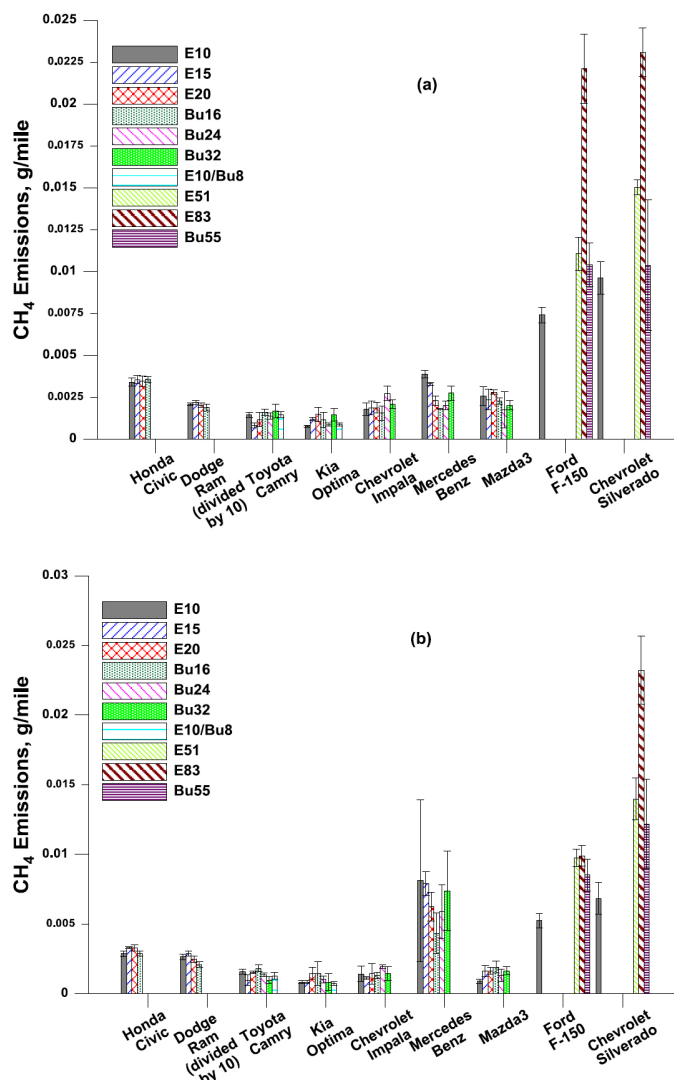


Figure 3. (a-b). CH₄ emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent $\pm$ one standard deviation around the average value for each fuel.