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# 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, CO<sub>2</sub>, PM mass, and particle number, and lower fuel economy with higher alcohol content fuels. For other pollutants, such as THC, NMHC, CH<sub>4</sub>, and NO<sub>x</sub>, 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 Ratcliff et al.

[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  $\text{NO}_x$ , 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  $\text{NO}_x$  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 conducted 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 40% fills and one 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<sub>x</sub>, NMHC, and CO<sub>2</sub>. NMHC was determined from the combined results from the THC analyzer and a separate CH<sub>4</sub> 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 C<sub>4</sub>-C<sub>12</sub> 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 cm<sup>3</sup>. 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 $CH_4$ 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.

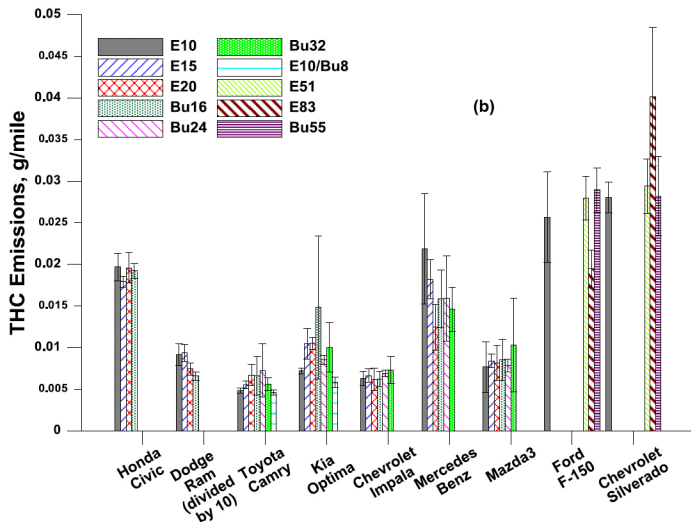
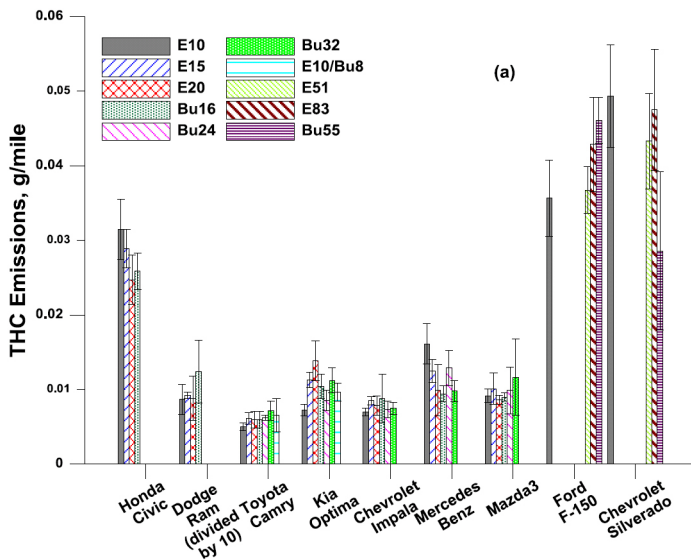


Figure 1. (a-b). THC emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

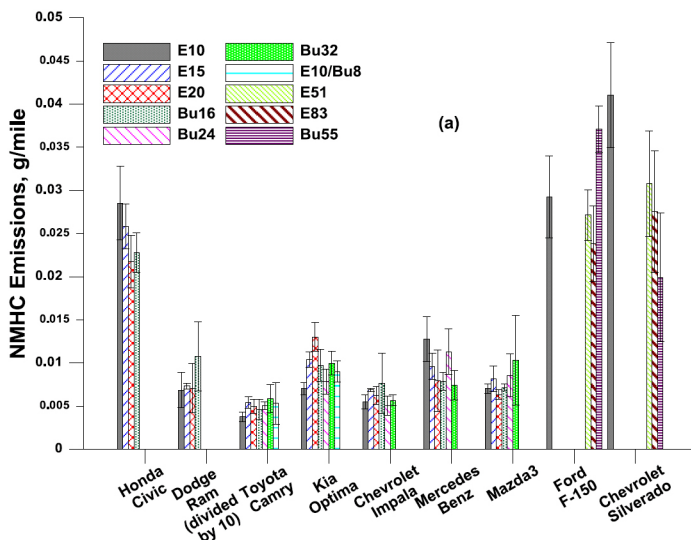


Figure 2. (a-b).

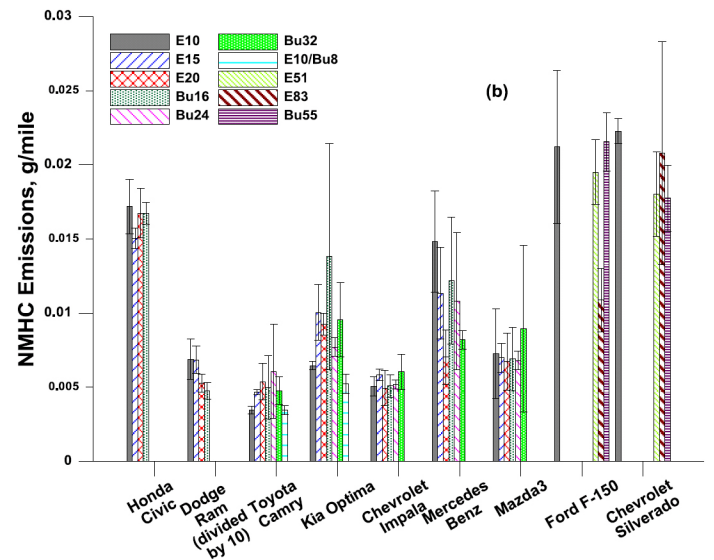


Figure 2. (a-b). (cont.) NMHC emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

Although the emissions of  $\text{CH}_4$  can contribute significantly to total  $\text{CO}_2$ -equivalent GHG emissions,  $\text{CH}_4$  emissions from mobile sources are not regulated in the US, as opposed to the EU.  $\text{CH}_4$  is a more potent GHG compared to  $\text{CO}_2$ , with a potency 21 times greater than  $\text{CO}_2$  over 100 years, but  $\text{CH}_4$  emissions are generally very low compared to  $\text{CO}_2$  emissions. Emissions of  $\text{CH}_4$  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),  $\text{CH}_4$  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.

$\text{CH}_4$  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  $\text{CH}_4$  emissions showed strong fuel differences for the FTP and UC cycles. For the FFVs, weighted  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CH}_4$  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, CH<sub>4</sub> 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 CH<sub>4</sub> emissions. For the hot-running FTP CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> from SI combustion. The precursors of CH<sub>4</sub> formation are CH<sub>3</sub> and C<sub>8</sub>H<sub>18</sub>, which suggests that the addition of either ethanol or butanol to gasoline will inhibit the production of CH<sub>4</sub> via the C<sub>8</sub>H<sub>18</sub> decomposition pathway [39]. Under the present test conditions, our results did not reveal a global trend of lower CH<sub>4</sub> emissions with alcohol fuel formulations for the non-FFVs, but for the FFVs substantial increases in CH<sub>4</sub> emissions with E51, E83, and Bu55 compared to E10 were found. Cold-start CH<sub>4</sub> emissions were found to be somewhat higher compared to hot-running and hot-start phases for both cycles. The differences in CH<sub>4</sub> 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 CH<sub>4</sub> is a more inert gas in terms of its oxidation activity in the TWC. So, the reductions in CH<sub>4</sub> 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.

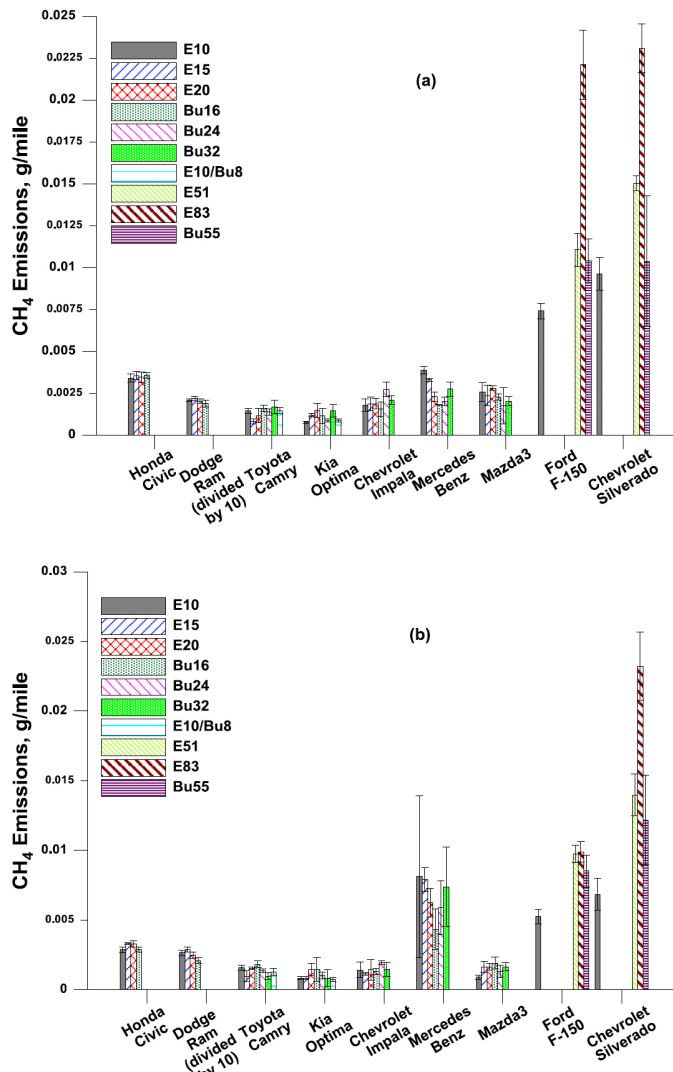


Figure 3. (a-b). CH<sub>4</sub> emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.



## NO<sub>x</sub> Emissions

NO<sub>x</sub> emissions as a function of fuel type are shown in Figure 4 (a, b) for the FTP and UC cycles. The NO<sub>x</sub> emissions for the Honda Civic, Toyota Camry, the SIDI vehicles, and the FFVs were about an order of magnitude lower than those for the Dodge Ram. For both the non-FFVs and FFVs, there were no statistically significant differences between fuels for the weighted emissions, of the FTP or UC cycle, and for the individual bag emissions only the NO<sub>x</sub> emissions for bag 3 for the non-FFVs showed statistically significant or marginally statistically significant differences. For the hot-start NO<sub>x</sub> emissions, for the non-FFVs, E20 and Bu16 blends showed statistically significant increases of 62% ( $p=0.0080$ ) and 52% ( $p=0.0341$ ), respectively, compared to E10, while a marginally statistically significant increase of 53% ( $p=0.0754$ ) for Bu32 was seen compared to E10.

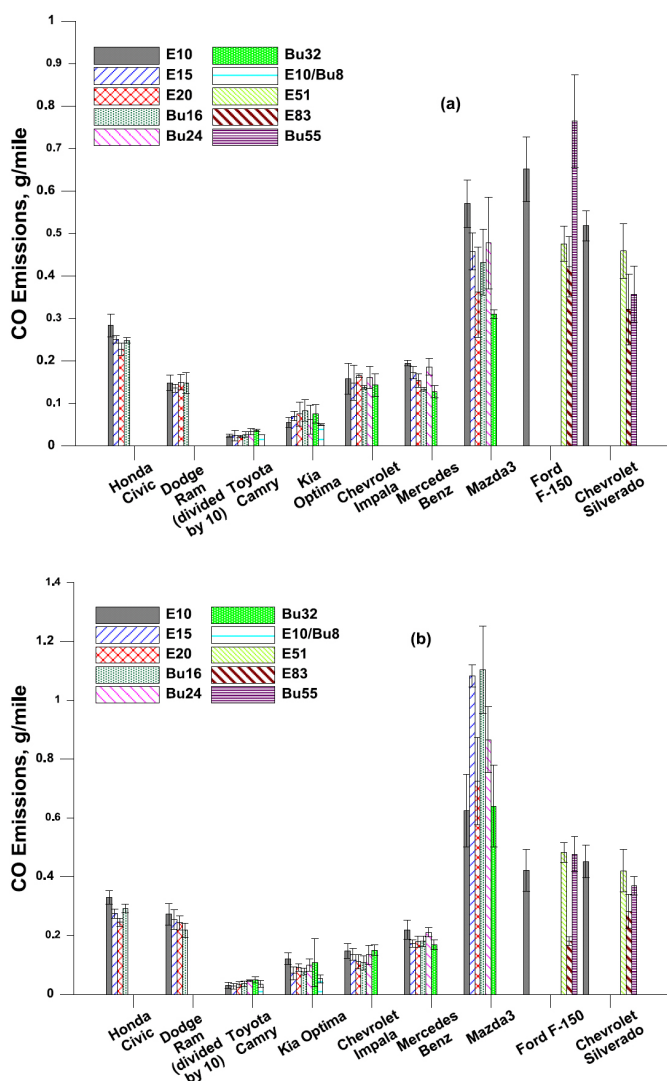


Figure 4. (a-b). NO<sub>x</sub> emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

## CO Emissions

Figure 5 (a, b) present the influence of ethanol and iso-butanol addition on CO emissions for both cycles. CO emissions showed some strong fuel trends, with statistically significant or marginally statistically significant differences for the weighted emissions for both the non-FFVs and the FFVs. For the non-FFVs, weighted CO emissions showed a marginally statistically significant reduction of 23% ( $p=0.0836$ ) for E10/Bu8 compared to E10 and a statistically significant reduction of 27% ( $p=0.0223$ ) for E10/Bu8 compared to Bu24. For the FFVs, weighted CO emissions showed a statistically significant reduction of 43% ( $p\leq 0.0001$ ) for E83 compared to E10, E83 showed a statistically significant decrease of 38% ( $p\leq 0.0001$ ) compared to E51, and Bu55 showed a statistically significant increase of 63% ( $p\leq 0.0001$ ) compared to E83.

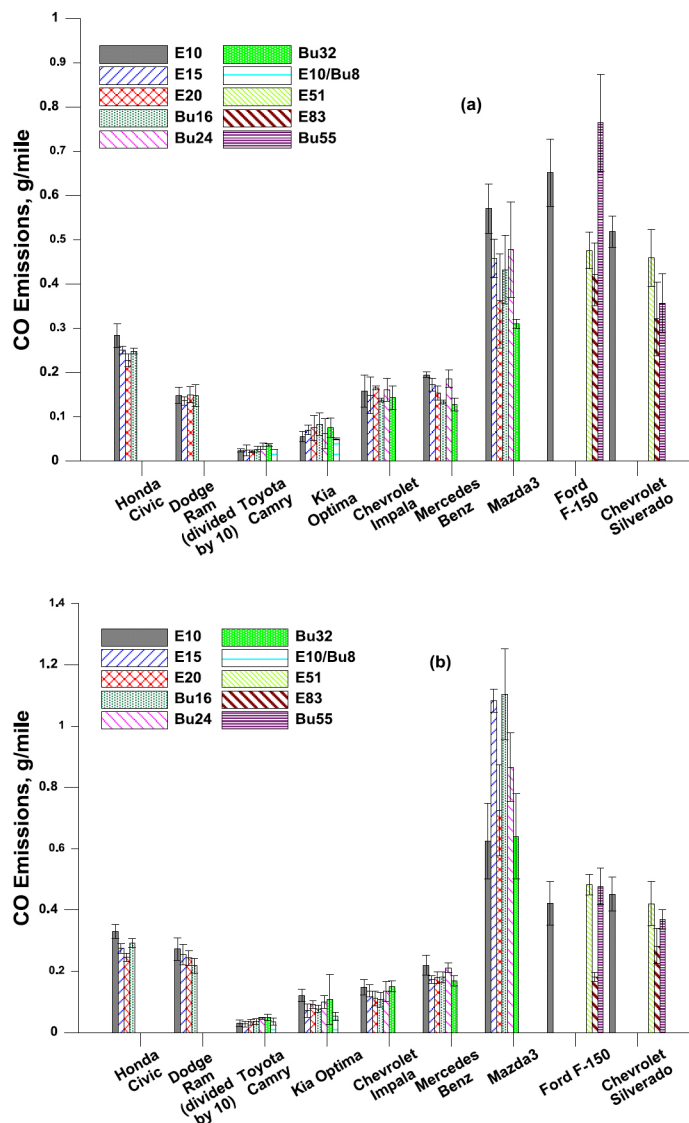


Figure 5. (a-b). CO emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

CO emissions showed some of the strongest fuel trends at a statistically significant level during the cold-start phases of the FTP and UC cycles for both the non-FFVs and the FFVs. For the cold-start FTP CO emissions, for the non-FFVs, Bu32 showed statistically significant decreases of 24% ( $p=0.0077$ ) and 21% ( $p=0.0291$ ), respectively, compared to E10 and E15, while marginally statistically significant decreases of 19% ( $p=0.0724$ ) and 21% ( $p=0.0961$ ), respectively, were seen for Bu32 compared to Bu16 and Bu24. For the cold-start UC CO emissions, the alcohol mixture E10/Bu8 showed statistically significant reductions of 39% ( $p=0.0167$ ), 43% ( $p=0.0038$ ), 40% ( $p=0.0137$ ), 43% ( $p=0.0032$ ), and 43% ( $p=0.0045$ ), respectively, compared to E15, E20, Bu16, Bu24, and Bu32 blends. For the FFVs, cold-start CO emissions showed statistically significant reductions of 40% ( $p=0.0011$ ) and 36% ( $p=0.0064$ ), respectively, for E83 compared to E10 and E51. The blend of Bu55 also showed a 59% ( $p=0.0036$ ) increase in cold-start CO emissions compared to E83 at a statistically significant level.

For the non-FFVs, the hot-running and hot-start CO emissions did not show any strong fuel effects, as opposed to the FFVs. For the FFVs, for the hot-running FTP CO emissions, a marginally statistically significant increase of 135 percent ( $p=0.0560$ ) was seen for Bu55 relative to E10. For the hot-running UC CO emissions, E83 showed statistically significant decreases of 55 percent ( $p=0.0006$ ) and 58 percent ( $p=0.0002$ ), respectively, compared to E10 and E51, and Bu55 showed an increase of 84 percent ( $p=0.0071$ ) compared to E83, at a statistically significant level. For the hot-start CO emissions, E83 showed a statistically significant decrease of 57 percent ( $p=0.0136$ ) relative to E10.

The general trend toward lower CO emissions with the higher alcohol fuel blends is consistent with previous studies that have shown reductions in CO with increasing alcohol content due to improved oxidation of the CO as a result of the oxygen content in the fuel [21,37,40]. For some vehicles, it was observed that the higher CO reductions were achieved with E20, E51, and E83 blends relative to E10. While it is hypothesized that the oxygen content was the primary contributing factor for the CO decrease, it might be possible that the CO decreases with the higher ethanol blends could be also a result of the considerably lower 50% distillation temperature (T50) compared to the other blends. This is in agreement with a previous study conducted by Durbin et al. [38] where they found reduced CO emissions with lowering T50 in ethanol blends. This is also in agreement with the findings of the EPAAct study, which showed that both a combination of fuel-borne oxygen and lower T50 were responsible for lower CO emissions on a fleet of PFI vehicles when running on ethanol blends [41]. It should be emphasized that similar to THC/NMHC emissions, CO emissions were dominated by the cold-start portion of the FTP and UC test cycles. The significantly higher CO emissions during cold-start compared to hot-running and hot-start emissions suggest that the combustion was rich during the first 200-300 seconds of the test cycles in addition to the catalyst being below its light-off temperature.

## CO<sub>2</sub> Emissions and Fuel Economy

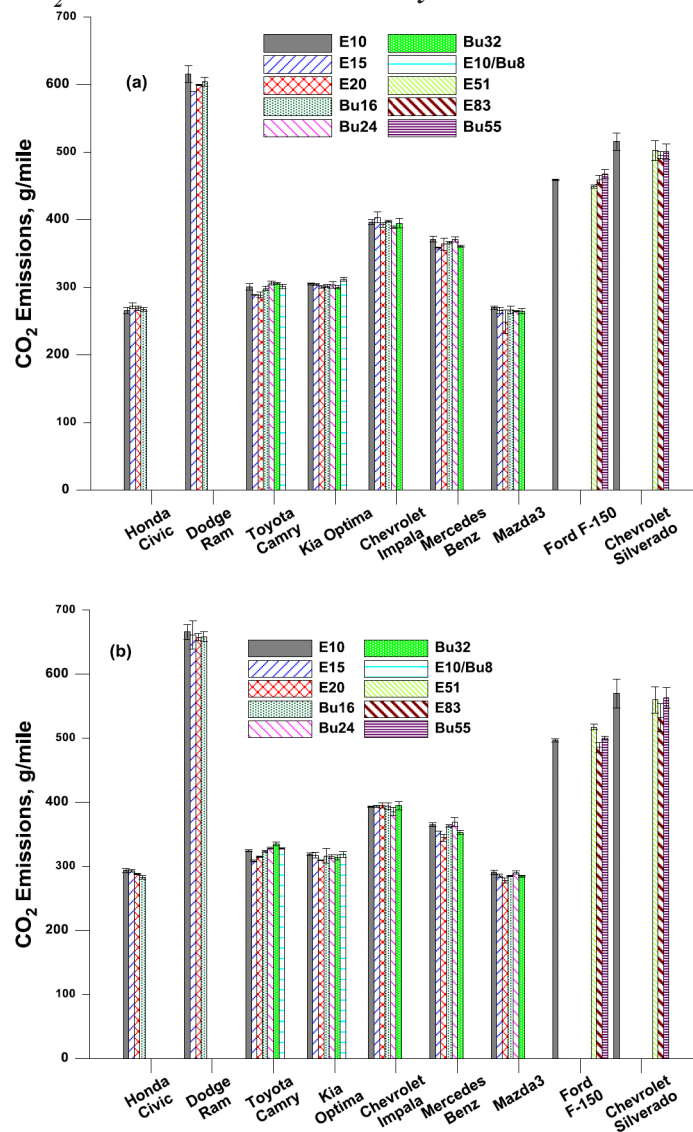


Figure 6. (a-b). CO<sub>2</sub> emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent ± one standard deviation around the average value for each fuel.

Figure 6 (a, b) shows the effect of alcohol type and concentration on the CO<sub>2</sub> emissions for the test vehicles over the FTP and UC. Weighted CO<sub>2</sub> emissions did show some statistically significant differences for both the non-FFVs and FFVs. For the non-FFVs, weighted CO<sub>2</sub> emissions showed a statistically significant decrease of 3% ( $p=0.0009$ ) for E20 relative to E10, whereas Bu24 and E10/Bu8 showed statistically significant increases of 3% ( $p=0.0106$ ) and 3% ( $p=0.0154$ ), respectively, and Bu32 a marginally statistically significant increase of 2% ( $p=0.0906$ ) compared to E20. For the FFVs, weighted CO<sub>2</sub> emissions did not show any strong trends between fuels for the FTP cycle, whereas for the UC some statistically significant and marginally significant differences for the fuels tested were observed. For the FFVs, E83 showed statistically significant decreases in weighted CO<sub>2</sub> emissions of 4% ( $p=0.0490$ ) and 6% ( $p=0.0107$ ), respectively, compared to E10 and E51, while Bu55 showed a marginally statistically significant increase of 4% ( $p=0.0655$ ) compared to E83. From a theoretical standpoint, it might

be expected that CO<sub>2</sub> emissions would trend with the carbon/hydrogen ratio in the fuel, with higher CO<sub>2</sub> emissions for fuels with higher carbon/hydrogen ratios. This is consistent with the results that showed some reductions for the higher alcohol blends, which have lower carbon/hydrogen ratios, but it was not consistent for the different segments or bags of the test cycles, or for many of the different vehicle/cycle combinations.

For the non-FFVs, for the cold-start CO<sub>2</sub> emissions, E20 showed a statistically significant reduction of 2% ( $p=0.0271$ ) relative to E10, while the butanol blends of Bu16, Bu24, and Bu32 showed statistically significant increases in CO<sub>2</sub> emissions of 2% ( $p=0.0453$ ), 5% ( $p\leq 0.0001$ ), and 4% ( $p=0.0006$ ), respectively, compared to E20. For the FFVs, for the cold-start CO<sub>2</sub> emissions, E83 showed a statistically significant decrease of 3% ( $p=0.0489$ ) relative to E10, and Bu55 showed a statistically significant increase of 3% ( $p=0.0438$ ) relative to E83. For the hot-running CO<sub>2</sub> emissions, for the non-FFVs, the only significant difference was observed between the E10 and E20 blends, with E20 showing a 2% ( $p=0.0598$ ) reduction in CO<sub>2</sub> emissions compared to E10 at a marginally statistically significant level. For the FFVs, E83 showed statistically significant reductions in CO<sub>2</sub> emissions of 4% ( $p=0.0162$ ) and 6% ( $p=0.0007$ ), respectively, compared to E10 and E51, while Bu55 showed a statistically significant increase of 4% ( $p=0.0374$ ) compared to E83. For the hot-start CO<sub>2</sub> emissions, the FFVs did not show any statistically significant effects between fuels for the FTP or UC cycles, while the non-FFVs showed some statistically significant differences between some fuels. For the non-FFVs, hot-start CO<sub>2</sub> emissions for E20 showed a statistically significant reduction of 2% ( $p=0.0193$ ) relative to E10 and Bu24 showed a statistically significant increase of 2% ( $p=0.0147$ ) relative to E20.

Fuel economy for each vehicle/fuel combination is presented in Figure 7 (a, b). Fuel economy was calculated based on the carbon balance method and the unique properties for each different test fuel and not according to the standard EPA equation. The carbon balance equation more directly accounts for the differences in energy content between different fuels, which are somewhat normalized out in the standard EPA equation. The fuel economy showed trends consistent with the energy differences in the fuels. In comparison with the E10 fuel, the E15, E20, Bu16, B24, Bu32, E51, E83, and Bu55 fuels had energy contents that were lower by 3.0%, 5.6%, 1.5%, 1.7%, 3.0%, 14.5%, 27.6%, and 7.6%, respectively.

Both the non-FFVs and the FFVs showed statistically significant fuel differences for fuel economy. For the weighted fuel economy, the FFVs showed the strongest fuel trends when compared to the conventional non-FFVs. For the non-FFVs, statistically significant decreases in weighted fuel economy of 2% ( $p=0.0455$ ) were found for E20 compared to E10, and of 3% ( $p=0.0041$ ), 4% ( $p\leq 0.0001$ ), and 4% ( $p=0.0075$ ), respectively, for Bu24, Bu32, and E10/Bu8 compared to Bu16. The blend of Bu32 also showed a decrease in weighted fuel economy of 2% ( $p=0.0544$ ) relative to E10, but at a marginally statistically significant level. The blend of Bu16 showed statistically significant increases in weighted fuel economy of 3% ( $p=0.0031$ ) and 4% ( $p\leq 0.0001$ ), respectively, compared to E15 and E20, and a marginally statistically significant increase of 2% ( $p=0.0945$ ) compared to E10. For the FFVs, weighted fuel economy showed

statistically significant reductions of 13 percent ( $p\leq 0.0001$ ), 24% ( $p\leq 0.0001$ ), and 7% ( $p\leq 0.0001$ ), respectively, for E51, E83, and Bu55 compared to E10. The blend of E83 also showed a statistically significant reduction in weighted fuel economy of 12% ( $p\leq 0.0001$ ) relative to E51, while weighted fuel economy for Bu55 was higher at a statistically significant level by 7% ( $p\leq 0.0001$ ) and 22% ( $p\leq 0.0001$ ) compared to E51 and E83, respectively.

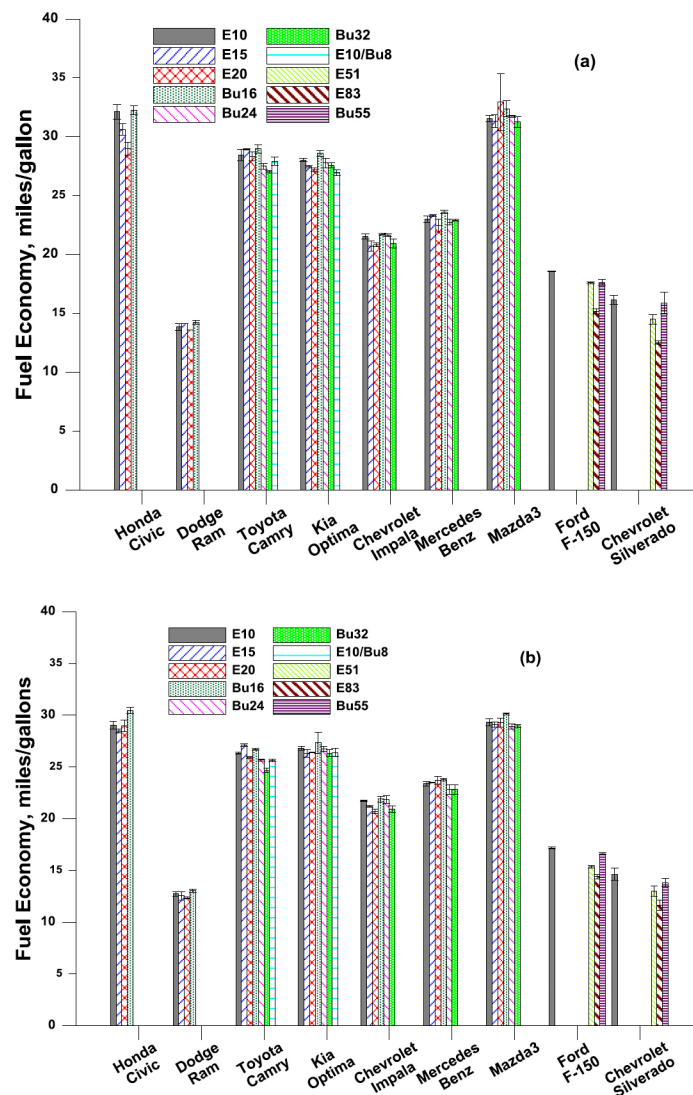


Figure 7. (a-b). Carbon balance fuel economy for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

For the cold-start fuel economy, there were no significant fuel effects for the conventional non-FFVs, while for the FFVs some strong fuel trends were observed for both the FTP and UC cycles. For the cold-start fuel economy, for the FTP, fuels E51, E83, and Bu55 showed statistically significant reductions of 16% ( $p\leq 0.0001$ ), 29% ( $p\leq 0.0001$ ), and 11% ( $p\leq 0.0001$ ), respectively, compared to E10, while E83 showed a statistically significant reduction of 16% ( $p\leq 0.0001$ ) compared to E51. Similar to weighted fuel economy, Bu55 showed statistically significant increases of 5% ( $p=0.0401$ ) and 25% ( $p\leq 0.0001$ ), respectively, compared to the E51 and E83 blends. For the UC, fuel economy showed statistically significant

reductions of 33% ( $p \leq 0.0001$ ), 40% ( $p \leq 0.0001$ ), and 28% ( $p = 0.0003$ ), respectively, for E51, E83, and Bu55 compared to E10, while Bu55 showed a statistically significant increase of 19% ( $p = 0.0129$ ) compared to E83. For the hot-running phase for the non-FFVs, fuel economy showed a marginally statistically significant increase of 3% ( $p = 0.0924$ ) and a statistically significant increase of 4% ( $p = 0.0012$ ) for Bu16 compared to E15 and E20, respectively. Fuel economy for Bu32 and E10/Bu8 showed a statistically significant decrease of 4% ( $p = 0.0038$ ) and a marginally statistically significant decrease of 4% ( $p = 0.0692$ ), respectively, compared to Bu16. For the FFVs, hot-running fuel economy for E51, E83, and Bu55 showed statistically significant decreases of 13% ( $p \leq 0.0001$ ), 24% ( $p \leq 0.0001$ ), and 7% ( $p = 0.0003$ ), respectively, compared to E10, while E83 showed a statistically significant decrease of 12% ( $p \leq 0.0001$ ) compared to E51. The Bu55 blend showed statistically significant increases in fuel economy of 8% ( $p \leq 0.0001$ ) and 23% ( $p \leq 0.0001$ ), respectively, compared to E51 and E83. For the hot-start phase, the non-FFVs did not show any strong trends in fuel economy between the fuel blends for the FTP or UC cycles. For the FFVs, hot-start fuel economy for E51 and E83 showed statistically significant decreases of 15% ( $p = 0.0315$ ) and 26% ( $p \leq 0.0001$ ), respectively, compared to E10, while E83 showed a statistically significant decrease of 13% ( $p = 0.0325$ ) compared to E51. The Bu55 blend showed a statistically significant increase in fuel economy of 18% ( $p = 0.0065$ ) compared to E83.

### PM Mass and Particle Number Emissions

The cumulative PM mass emissions are shown in Figure 8 (a, b). PM mass was only collected for the Toyota Camry, the SIDI vehicles, and the FFVs. It should be noted that for the Toyota Camry, PM mass emissions were found to be below the tunnel background levels for most fuel blends for the FTP. Overall, PM emission results showed reductions with higher oxygen levels for a number of the vehicle/cycle combinations.

PM mass emissions showed some strong differences between fuels for both the conventional non-FFVs and the FFVs. For the non-FFVs, PM mass emissions Bu16 and Bu24 showed increases of 81% ( $p = 0.0901$ ) and 94% ( $p = 0.0176$ ) compared to E20 at marginally statistically significant and statistically significant levels, respectively. For the FFVs, PM mass emissions did not show any fuel effect over the FTP cycle, but showed some significant differences during UC operation. For the UC, PM mass emissions for E51, E83, and Bu55 showed statistically significant decreases of 61% ( $p = 0.0083$ ), 59% ( $p = 0.0114$ ), and 52% ( $p = 0.0114$ ), respectively, compared to E10.

Higher PM emissions for the SIDI fueled vehicles are expected and have been reported in previous studies [14,16]. Our results are also in agreement with a more recent study of PFI vehicles of model year 2005 and newer, which show PM mass rates of  $< 1$  mg/mile over the FTP [15]. Elevated PM mass emissions from SIDI vehicles can be ascribed to insufficient homogeneous mixtures and subsequent fuel evaporation, wall wetting, and a less efficient mixing of air and fuel compared to PFI vehicles, where the fuel is injected and vaporized into the intake ports [42]. In addition, the higher PM emissions from the SIDI vehicles were predominantly released from the cold-start phase where cold piston and cylinder surfaces exacerbate liquid fuel

impingement and reduce evaporation from surfaces, which produces soot when the fuel ignites [43]. The substantially lower PM mass emissions for the spray-guided vehicle as compared to the wall-guided vehicles could be ascribed to the higher injection pressure, relatively better mixture preparation, and reduced impingement of fuel on the combustion chamber surfaces [42].

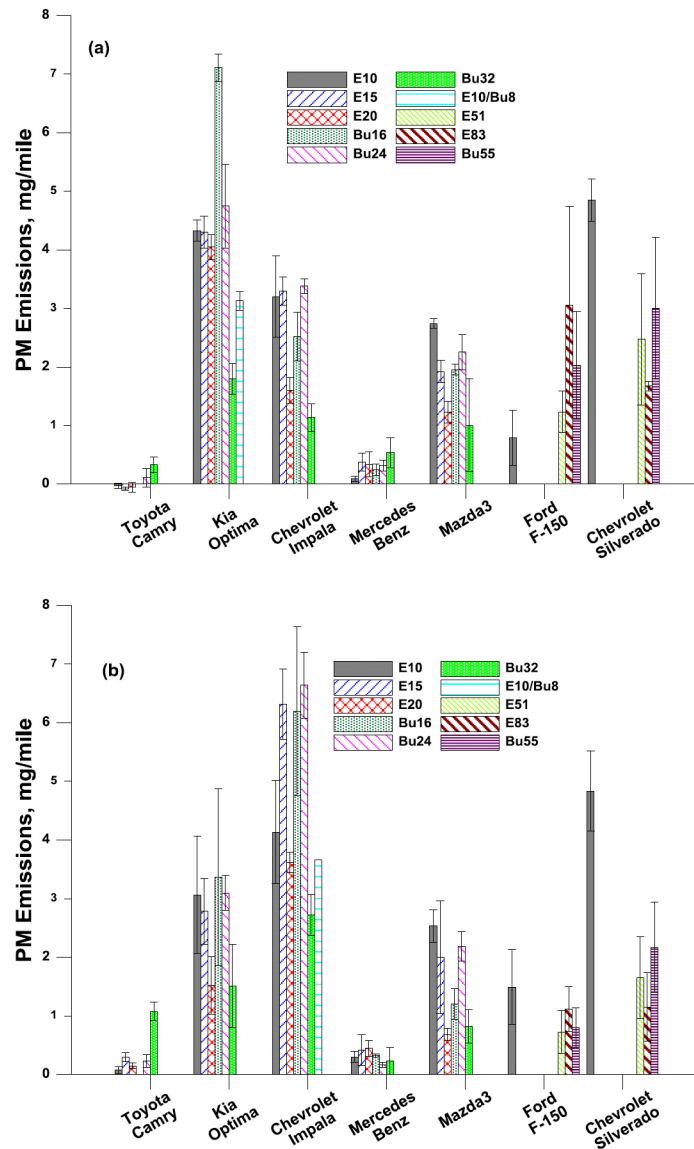


Figure 8. (a-b). PM mass emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

The total particle number emissions are displayed in Figure 9 (a, b). For most vehicles, particle number emissions corroborate the PM mass trends, with the exception of the PFI Ford F-150. In general, the SIDI vehicles exhibited significantly higher particle number counts compared to their PFI counterparts, noting that the PN emissions for the PFI vehicles are multiplied by a factor in the graphs. It is interesting to note that the PFI Ford F-150 FFV produced similar particle number counts to the spray-guided Mercedes Benz. The lower particle number emissions for PFI vehicles can be attributed to the better mixture preparation of PFI engines in relation to SIDI engines and the likelihood of fuel impingement onto the piston for

the SIDI engines. This may result in liquid fuel that is not totally vaporized at the start of combustion. As a consequence, local fuel-rich combustion or even pool fires can occur near the piston, generating high particle emissions [42,44]. Overall, the more aggressive driving conditions for the UC increased particle number counts for all vehicle/fuel combinations compared to the FTP. As previously discussed, the main contributing factors for the lower particle number emissions for the spray-guided SIDI vehicle as compared to the wall-guided SIDI vehicles, could be the reduced time for mixture preparation and less fuel wetting.

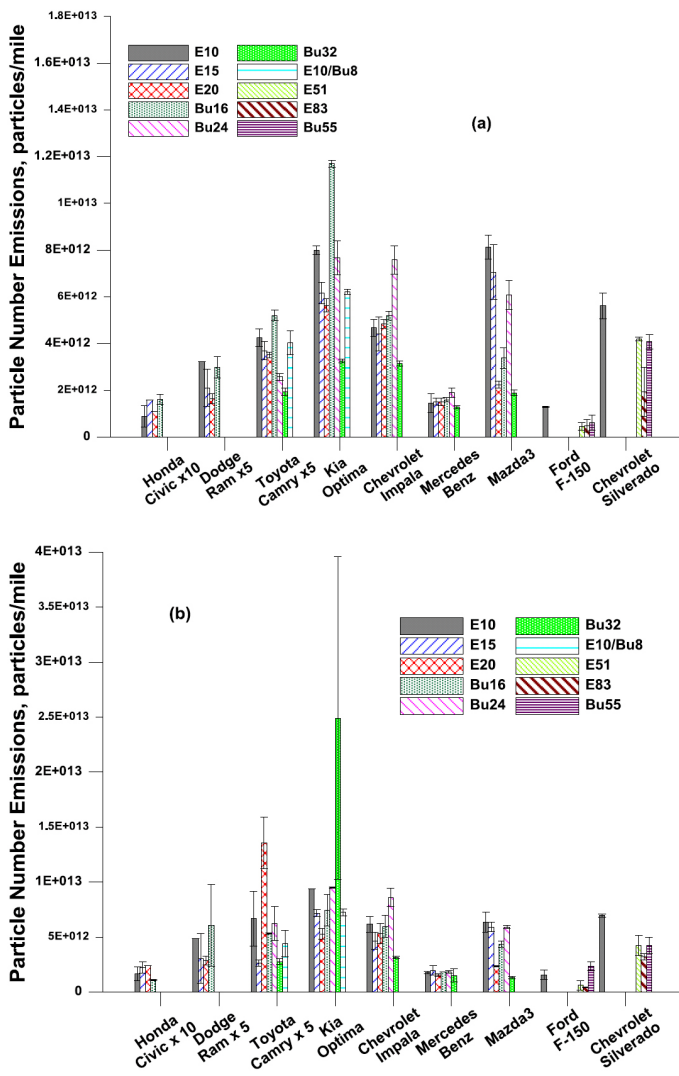


Figure 9. (a-b). Particle number emissions for all vehicle/fuel combinations over the FTP (a) and UC (b) cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

Weighted particle number emissions showed fuel impacts for both the non-FFVs and the FFVs. For the non-FFVs, particle number emissions showed a marginally statistically significant decrease of 25% ( $p=0.0856$ ) for E20 compared to E10 and statistically significant decreases of 47% ( $p\leq 0.0001$ ) and 37% ( $p=0.0005$ ), respectively, for Bu32 compared to E10 and E15. The Bu32 blend also showed statistically significant decreases in particle number emissions of 50% ( $p\leq 0.0001$ ) and 51% ( $p\leq 0.0001$ ), respectively, compared to Bu16 and Bu24 blends. The Bu16 and Bu24 blends showed statistically

significant increases in particle number emissions of 43% ( $p=0.0062$ ) and 46% ( $p=0.0083$ ), respectively, whereas Bu32 showed a statistically significant decrease of 29% ( $p=0.0274$ ) compared to E20. For the FFVs, weighted particle number emissions for E51 and E83 showed statistically significant decreases of 51% ( $p=0.0029$ ) and 57% ( $p=0.0001$ ), respectively, compared to E10, while Bu55 showed a statistically significant increase in particle number emissions of 75% ( $p=0.0154$ ) compared to E83.

In addition to the weighted particle number emissions, strong differences between the fuels for the FTP or the UC cycles were also observed during the cold-start, hot-running, and hot-start phases for both the non-FFVs and FFVs. For the non-FFVs, cold-start particle number emissions showed some strong fuel trends over the UC but not over the FTP. For the UC, cold-start particle number emissions for E20 and Bu32 showed reductions of 36% ( $p=0.0685$ ) and 41% ( $p=0.0122$ ), respectively, compared to E10 at marginally statistically significant and statistically significant levels. Statistically significant reductions in cold-start particle number emissions were also seen for Bu32 of the order of 40% ( $p=0.0126$ ) and 47% ( $p=0.0014$ ), respectively, compared to Bu16 and Bu24 blends. Cold-start particle number emissions also showed increases of 56% ( $p=0.0651$ ) and 74% ( $p=0.0161$ ), respectively, for Bu24 compared to E15 and E20, at statistically significant and marginally statistically significant levels. Fuel Bu16 also showed a marginally statistically significant increase of 52% ( $p=0.0759$ ) relative to E20. For the FFVs, cold-start particle number emissions for E51 and E83 showed reductions of 48% ( $p=0.0726$ ) and 68% ( $p=0.0003$ ), respectively, relative to E10 at marginally statistically significant and statistically significant levels. The Bu55 blend showed a statistically significant increase in cold-start particle number emissions of 127% ( $p=0.0110$ ) compared to E83. For the hot-running particle number emissions, for the non-FFVs, Bu32 showed statistically significant decreases of 51% ( $p=0.0073$ ), 49% ( $p=0.0137$ ), and 52% ( $p=0.0069$ ), respectively, compared to E10, Bu16, and Bu24 fuels. For the FFVs, hot-running particle number emissions for E51 and E83 showed statistically significant decreases of 47% ( $p=0.0138$ ) and 53% ( $p=0.0009$ ), respectively, compared to E10. For the hot-start particle number emissions, for the non-FFVs, E15, E20, and Bu32 showed statistically significant reductions of 32% ( $p=0.0348$ ), 34% ( $p=0.0166$ ), and 67% ( $p\leq 0.0001$ ), respectively, compared to E10. The Bu32 fuel also showed statistically significant reductions of 51% ( $p\leq 0.0001$ ), 50% ( $p\leq 0.0001$ ), 63% ( $p\leq 0.0001$ ), 56% ( $p\leq 0.0001$ ), and 67% ( $p\leq 0.0001$ ), respectively, compared to E15, E20, Bu16, B24, and the E10/Bu8 blend. For the FFVs, hot-start particle number emissions for E51, E83, and Bu55 showed statistically significant reductions of 56% ( $p=0.0004$ ), 59% ( $p\leq 0.0001$ ), and 51% ( $p=0.0010$ ), respectively, compared to E10.

Particle number results reported here generally decreased with the addition of ethanol and iso-butanol, implying that the presence of oxygen in the fuel was the main contributing factor for the particle number decrease by suppressing soot formation [27, 28, 32, 36, 44, 45]. In addition to the oxygen content, particulate emissions are also strongly related to the aromatic hydrocarbons content in the fuel [46]. The addition of higher blends of ethanol and iso-butanol in gasoline decreased the fraction of aromatic hydrocarbons and therefore their propensity of forming soot. The effect of aromatics

on particle number emissions was particularly strong for the higher ethanol blends and the iso-butanol blend rather than the low- and mid-level alcohol blends where fuel aromatics were relatively controlled for most blends. This is consistent with the findings of Wallner and Frazee [34], which showed that the reduction in the availability of carbon in ethanol combustion decreases the potential for benzene and soot formation as the ethanol blend ratio increases. It is interesting to note that in some cases the iso-butanol blends had higher particle number emissions compared to their corresponding ethanol blends, with the exception of Bu32, which emitted the lowest particle number emissions for most vehicles and could be a consequence of its lower monoaromatics and multi-substituted aromatics content. This phenomenon could be attributed to the fact that during combustion branched butanols can produce intermediate products, such as propene and butene, leading to the formation of more benzene and soot [47]. The results of this study indicate that the degree of branching (iso-butanol versus ethanol) may have an impact on soot formation in addition to oxygen content, since the intermediate butanol blends had equivalent oxygen contents to their corresponding ethanol blends. In addition to fuel structure, the higher viscosity of butanol blends relative to ethanol blends could also have influenced particle number emissions by altering the fuel spray characteristics [48].

### Carbonyl Emissions

Carbonyl emissions are displayed in Figures 10, 11, 12, 13. For better representation of the results, the vehicles have been grouped based on their type. Figure 10, 11, 12 shows the carbonyl emissions for the non-FFV PFI vehicles and the non-FFV SIDI vehicles, while Figure 13 shows the carbonyl emissions for the FFVs. It should be noted that carbonyl emissions only measured over the FTP cycle and were collected cumulatively over the entire cycle. For all vehicle/fuel combinations, low molecular-weight aldehydes such as formaldehyde and acetaldehyde were the most abundant compounds in the tailpipe followed by butyraldehyde, benzaldehyde, propionaldehyde, crotonaldehyde, and methacrolein. Previous studies have also shown that lighter aldehydes, such as formaldehyde and acetaldehyde, were the dominant carbonyl compounds in vehicle exhaust [21,33,45].

Statistical analysis was performed to identify the fuel effects on the emissions of formaldehyde, acetaldehyde, and butyraldehyde. For the non-FFVs, the fuel blends did not show any statistically significant effect on formaldehyde and acetaldehyde emissions. Our results showed both increases and decreases in both aldehydes for most vehicles without consistent trends. For the FFVs, on the other hand, the fuel impact on carbonyl emissions was particularly strong, especially for acetaldehyde emissions. For formaldehyde emissions, there were some increases for the PFI Ford F-150 with the higher alcohol fuels, but not for the SIDI Chevrolet Silverado. Marginally statistically significant differences in formaldehyde emissions were only seen for Bu55, which increased on the order of 49% ( $p=0.0957$ ) compared to E51. As expected, acetaldehyde emissions showed stronger effects between fuels for the FFVs, especially for the higher ethanol blends. For acetaldehyde emissions, E51 and E83 showed statistically significant increases of 380% ( $p\leq 0.0001$ ) and 580% ( $p\leq 0.0001$ ), respectively, compared to E10, while Bu55 exhibited

statistically significant reductions in acetaldehyde emissions of 79% ( $p\leq 0.0001$ ) and 85% ( $p\leq 0.0001$ ), respectively, compared to E51 and E83 blends.

High molecular weight aldehydes, including benzaldehyde, crotonaldehyde, and propionaldehyde, were not included in the statistical analysis. These compounds showed both increases and decreases with higher ethanol and iso-butanol blends for the conventional PFI and SIDI vehicles and the FFVs. For benzaldehyde emissions, in general, the higher oxygen content/lower aromatics blends resulted in lower emissions than E10, without this trend being consistent. It was also appeared that higher concentration of iso-butanol favored the formation pathway of propionaldehyde compared to ethanol blends. This phenomenon was more pronounced for the FFVs where the use of Bu55 led to sharp increases in propionaldehyde emissions relative to ethanol fuels. Overall, methacrolein emissions trended lower with higher ethanol and butanol blends with some exceptions, indicating that neither ethanol nor butanol participate in the formation of this pollutant.

Generally, aldehydes and ketones form as a result of partial oxidation of the fuel components during combustion, as gasoline fuels do not contain carbonyl compounds. Previous studies have shown that the addition of ethanol and butanol fuels can produce higher formaldehyde and acetaldehyde emissions [21,24,34,40].

Formaldehyde is produced from oxygenated fuels and also by the decrease of fuel aromatics, since aromatics do not participate in the formation of formaldehyde [49]. For iso-butanol, formaldehyde is produced through the oxidation of methyl radicals to form  $\text{CH}_3\text{O}$  and hydroxyl radicals that in turn yield formaldehyde. Formaldehyde is also formed by  $\beta$ -scission decomposition of the  $\text{C}_4\text{H}_8\text{OH}$  radical [39,50]. Acetaldehyde is principally produced through the partial oxidation of ethanol [49]. Iso-butanol can also form acetaldehyde through the C-C bond scission reaction of iso-butanol and hydrogen atom abstraction from iso-butanol to produce  $\text{C}_4\text{H}_8\text{OH}$  radical, which further undergoes  $\beta$ -scission [51]. This formation pathway is not as strong as that for ethanol, however. McEnally and Pfeifferle [47] showed that branched butanols, through their fission produce hydroxyl-ethyl radicals, likely dissociate by  $\beta$ -scission of the O-H bond to produce acetaldehyde. Grana et al. [52] showed that the mole fraction of acetaldehyde is lower in the iso-butanol flame, which implies that there is a pathway for butanol fuels that destroys acetaldehyde and then creates formaldehyde. This is consistent with some of the trends seen in this study for the SIDI vehicles.

Butyraldehyde emissions appeared to be higher with the use of higher iso-butanol blends. This finding is in agreement with recent chassis dynamometer studies, which showed higher butyraldehyde emissions for butanol fuels [32, 33]. Statistical analyses showed that butyraldehyde emissions were different between fuels for the FTP or the UC test cycles for both the conventional non-FFVs and the FFVs.

For the non-FFVs, butyraldehyde emissions for Bu16 and B32 showed statistically significant increases of 672% ( $p=0.0167$ ) and 817% ( $p=0.0052$ ), respectively, compared to E20. For the FFVs, butyraldehyde emissions for Bu55 showed statistically significant increases of 261% ( $p=0.0039$ ), 626% ( $p\leq 0.0001$ ), and 269% ( $p=0.0034$ ), respectively, compared to E10, E51, and E83 blends. It

was assumed that butyraldehyde was formed via sequential H-atoms abstractions from the iso-butanol hydroxyl moiety to form a  $C_4H_9O$  radical, which then undergoes  $\beta$ -scission to yield butyraldehyde [53]. The increased butyraldehyde emissions for the higher butanol blends could be an important finding because butyraldehyde has reactivity and mutagenicity properties that are similar to those of acetaldehyde. For the FFVs, higher propionaldehyde emissions for Bu55 relative to the ethanol blends were also observed, which can be attributed its formation from 1-propanol via H and/or  $HO_2$  assisted enol-keto isomerization [50].

Benzaldehyde, which is primarily produced from fuel aromatic hydrocarbons, showed mixed trends with the alcohol fuels for the SIDI vehicles. Our results are in agreement with those studies showing that the addition of oxygenates generally decreases benzaldehyde emissions [21,27,39], but are also consistent with other studies showing some increases in benzaldehyde emissions probably because of the enhancement of aromatics oxidation [49]. We hypothesize that benzaldehyde can be produced from oxygen addition to alkyl branches of toluene, xylene, and trimethylbenzene present in gasoline.

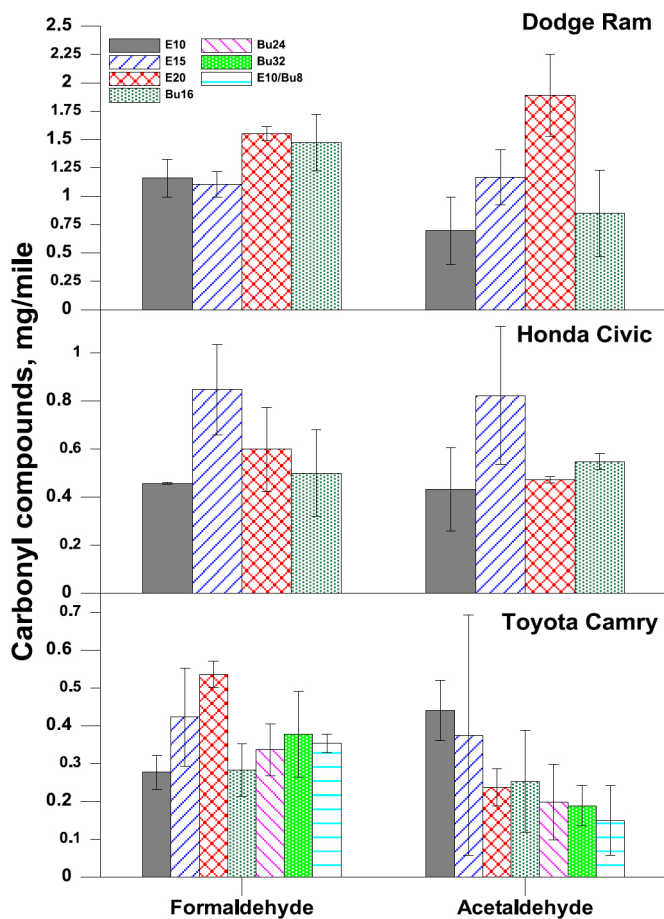


Figure 10. Formaldehyde and acetaldehyde emissions for the non-FFV PFI vehicles over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

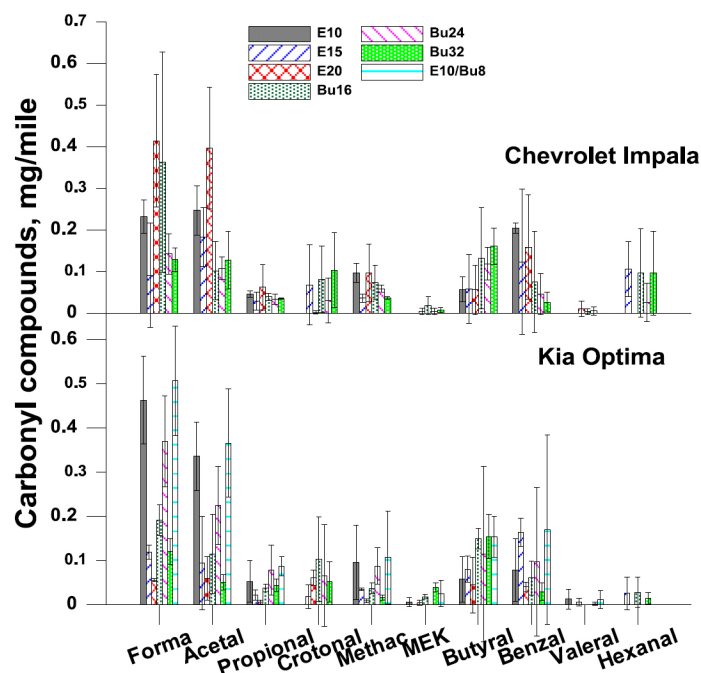


Figure 11. Carbonyl emissions for the SIDI Kia Optima and Chevrolet Impala vehicles over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

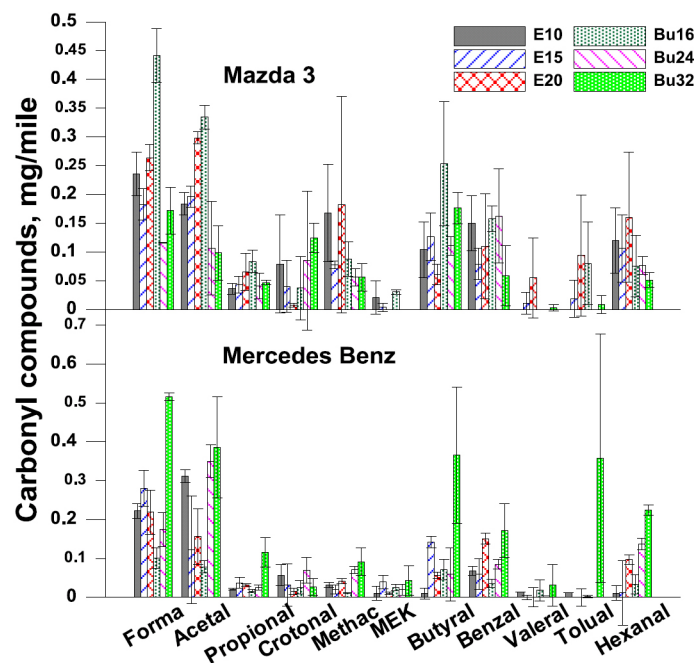


Figure 12. Carbonyl emissions for the SIDI Mercedes Benz and Mazda 3 vehicles over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

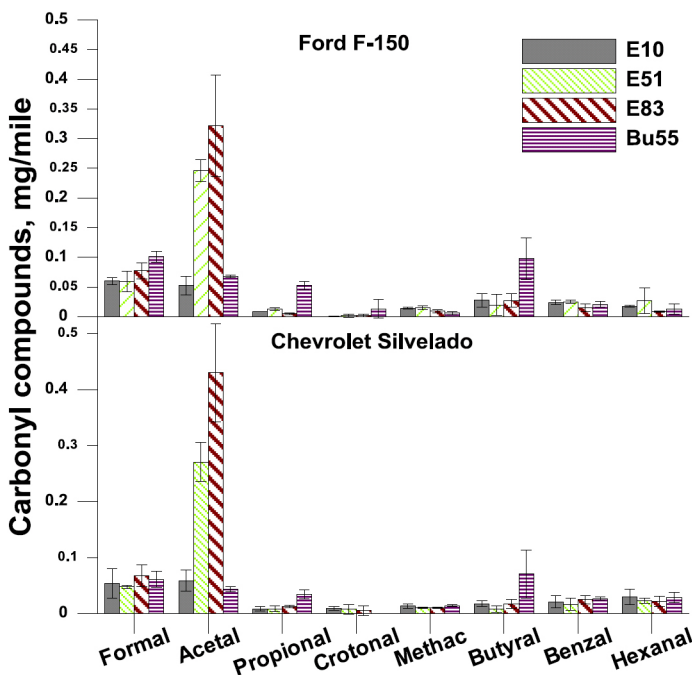


Figure 13. Carbonyl emissions for the FFVs over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

### Selected Volatile Hydrocarbons

Figure 14, Figure 15, Figure 16 show the selected volatile organic compounds (VOCs) for the non-FFV PFI vehicles and the non-FFV SIDI vehicles, while Figure 17 shows the selected VOCs for the FFVs. The compounds of 1,3-butadiene, benzene, ethylbenzene, toluene, *m/p*-xylene, and *o*-xylene were measured cumulatively only over the FTP cycle. The monoaromatic hydrocarbons of benzene, ethylbenzene, toluene, *m/p*-xylene, and *o*-xylene are commonly termed BTEX. The most reactive VOCs from internal combustion engines are BTEX compounds, since they contain a C=C bond, that can promote free radicals. The results show that toluene was the most abundant VOC, followed by benzene and *m/p*-xylene.

For benzene emissions, whose principal source is partial combustion of toluene and xylene, there were no statistical significant differences between the fuels for the non-FFVs, although some specific vehicles/fuel combinations did show fuel differences. More specifically the Honda Civic and Mercedes Benz showed lower benzene emissions with the higher ethanol blends compared to E10. The Kia Optima and Chevrolet Silverado showed some increases in benzene emissions with some higher alcohol blends relative to E10. For the FFVs, the fuel effect on benzene emissions was particularly clear with E83 showing statistically significant reductions of 60% ( $p=0.0048$ ) and 54% ( $p=0.0254$ ), respectively, compared to E10 and E51.

Toluene emissions did not show any strong fuel effects for the conventional PFI and SIDI vehicles. Some trends of higher toluene emissions were seen for the Kia Optima with increasing ethanol concentration in gasoline. On the other hand, the FFVs showed statistically significant differences in toluene emissions between the fuel blends. Toluene emissions showed statistically significant reductions of 66% ( $p=0.0049$ ) and 88% ( $p\leq 0.0001$ ), respectively, for E83 and Bu55 compared to E10. Statistically significant reductions in

toluene emissions were also seen for E83 (61%,  $p=0.0229$ ) and Bu55 (86%,  $p\leq 0.0001$ ) compared to E51, and Bu55 (65%,  $p=0.0064$ ) compared to E83.

Ethylbenzene emissions did not exhibit any significant differences between fuels for the non-FFVs with the exception of Bu32, which showed a 39% ( $p=0.0293$ ) reduction compared to Bu16 at a statistically significant level. For the FFVs, ethylbenzene emissions showed reductions with the use of higher alcohol blends, with most of these differences being statistically significant. The blends of E83 and Bu55 showed statistically significant reductions of the order of 79% ( $p\leq 0.0001$ ) and 77% ( $p=0.0001$ ), respectively, relative to E10, whereas E83 and Bu55 showed statistically significant reductions of the order of 84% ( $p\leq 0.0001$ ) and 82% ( $p\leq 0.0001$ ), respectively, compared to E51.

Emissions of *m/p*-xylene resulted in statistical significant differences for some fuels for the non-FFVs. It might be expected that the emissions of *m/p*-xylenes would decrease with the addition of higher ethanol and iso-butanol blends due to their lower monoaromatic content. Statistically significant reductions in *m/p*-xylene emissions for Bu32 of 41% ( $p=0.0005$ ), 33% ( $p=0.0193$ ), and 39% ( $p=0.0024$ ), respectively, were seen compared to the E20, Bu16, and Bu24 blends. On the other hand, a marginally statistically significant increase of 35% ( $p=0.0958$ ) was seen for E20 for in *m/p*-xylene emissions compared to E10. For *o*-xylene emissions for the non-FFVs, Bu32 showed statistically significant reductions of 32% ( $p=0.0421$ ), 35% ( $p=0.0086$ ), 42% ( $p=0.0005$ ), and 38% ( $p=0.0040$ ), respectively, compared to E15, E20, Bu16, and Bu24 blends. Similar to the conventional PFI and SIDI vehicles, the FFVs showed decreases in *m/p*-xylene emissions with the use of higher alcohol blends. Specifically, E83 and Bu55 showed statistically significant reductions in *m/p*-xylene emissions on the order of 84% ( $p\leq 0.0001$ ) and 74% ( $p=0.0003$ ), respectively, compared to E10 and of 72% ( $p=0.0004$ ) and 54% ( $p=0.0272$ ), respectively, compared to E51. A similar picture was also observed for *o*-xylene emissions with E83 and Bu55 showing statistically significant reductions of 77% ( $p\leq 0.0001$ ) and 75% ( $p=0.0002$ ), respectively, compared to E10, and 66% ( $p=0.0015$ ) and 64% ( $p=0.0026$ ), respectively, compared to E51.

Emissions of 1,3-butadiene, which is a classified carcinogenic compound to humans, were generally found at very low concentrations for all vehicle/fuel combinations compared to the monoaromatic VOCs. Although 1,3-butadiene did not show any statistical significant differences between fuels for the non-FFVs, some increases were seen for the butanol blends compared to the ethanol blends. For the FFVs, this trend was more pronounced, with the Bu55 blend showing a statistically significant increase of 318% ( $p=0.0162$ ) compared to E83. For iso-butanol, 1,3-butadiene can be formed from reactions with propargyl or vinyl radicals with ethane, or from the decomposition of the fuel itself.

Overall, the reductions in BTEX emissions for the higher ethanol blends and the iso-butanol blend can be primarily ascribed to the lower aromatic contents for these fuels compared to the baseline E10.



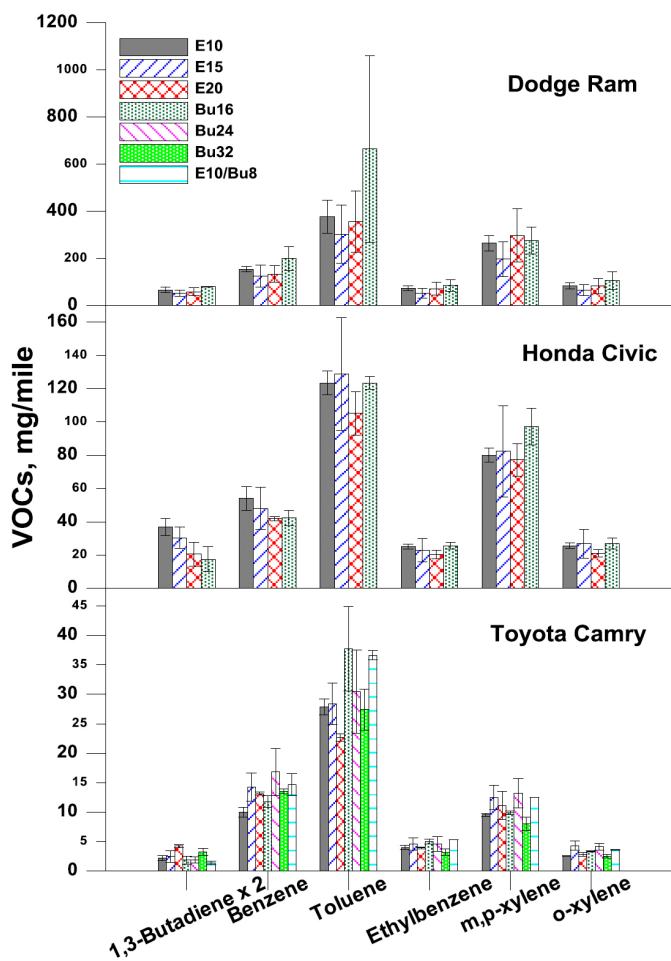


Figure 14. BTEX and 1,3-butadiene emissions for the non-FFV PFI vehicles over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

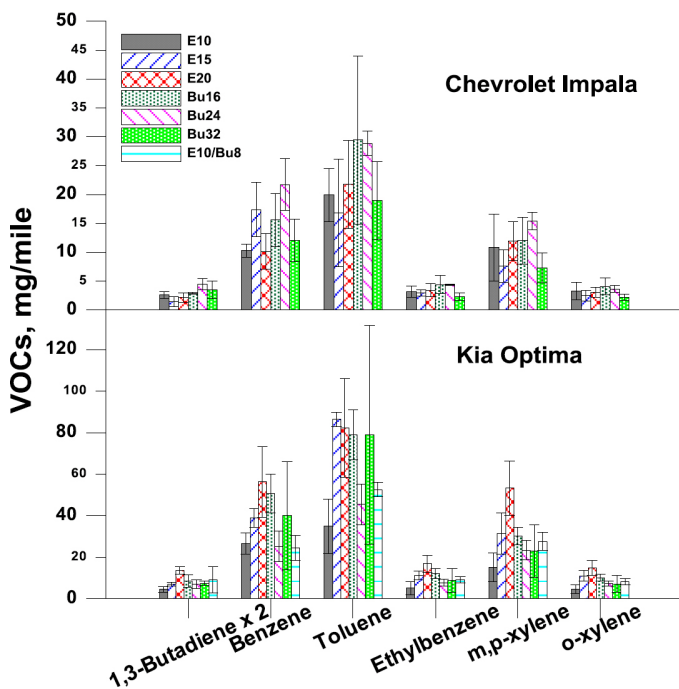


Figure 15. BTEX and 1,3-butadiene emissions for the non-FFV SIDI Kia Optima and Chevrolet Impala vehicles over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

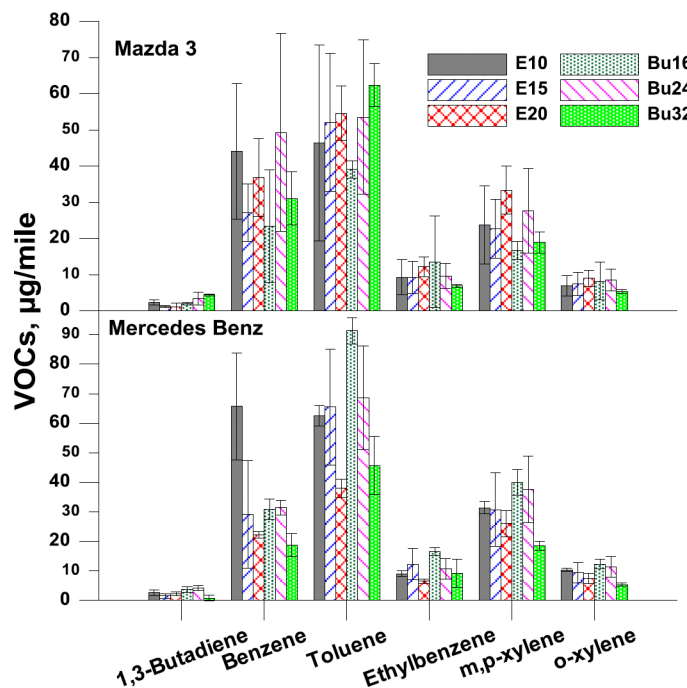


Figure 16. BTEX and 1,3-butadiene emissions for the non-FFV SIDI Mercedes Benz and Mazda 3 vehicles over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

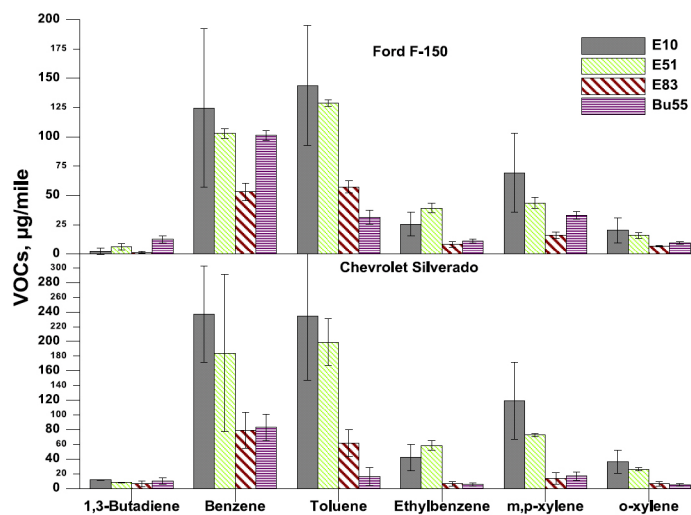


Figure 17. BTEX and 1,3-butadiene emissions for the FFVs over the FTP cycle; Errors bars represent  $\pm$  one standard deviation around the average value for each fuel.

## CONCLUSIONS

There is a growing need to evaluate the potential impacts of new fuels on the exhaust emissions for modern technology vehicles, and ultimately their effect on regional and global air quality, as the deployment of ethanol and potentially butanol fuels continues to expand in the gasoline pool along with more widespread penetration of direct injection gasoline vehicles. In this study, ten alcohol formulations including ethanol blends, iso-butanol blends, and an alcohol mixture were tested on a fleet of nine different light-duty vehicles ranged in model year from 2007-2014. A total of 48 different vehicle/fuel combinations were included in the test matrix. At each

test matrix point, the vehicles were run over 3 Federal Test Procedure (FTP) cycles and 3 Unified Cycles using a chassis dynamometer. The results of this study can be summarized as follows:

- Fuel effects showed mixed results for different vehicles and cycles for THC, NMHC, and NO<sub>x</sub> emissions and did not show any statistically significant differences for the weighted emissions for these pollutants. Cold-start THC and NMHC emissions were lower for the E10/Bu8 blend compared to most of the other blends for the non-FFVs.
- CH<sub>4</sub> weighted emissions for the FFVs were higher for the higher alcohol blends (E51, Bu55, and E83) compared to E10, and were higher for E83 compared to the E51 and Bu55 mid-level blends.
- There were some trends toward lower CO emissions with the higher alcohol fuel blends. For the FFVs, weighted and cold-start CO emissions were lower for E83 than the E10, E51, and Bu55 fuels. This is consistent with previous studies that have shown reductions in CO with increasing alcohol content due to improved oxidation of the CO as a result of the oxygen content in the fuel.
- CO<sub>2</sub> emissions showed some differences between different fuels, but not over all testing conditions. From a theoretical standpoint, it might be expected that CO<sub>2</sub> emissions would trend with the carbon/hydrogen ratio in the fuel, with lower CO<sub>2</sub> emissions for the higher alcohol blends with lower carbon/hydrogen ratios. This trend was seen for some fuel/cycle combinations, but not for others. The main effects were that E20 had lower CO<sub>2</sub> emissions than other fuels for the non-FFVs, and that the E83 fuel had lower emissions than the other fuels for the FFVs.
- Fuel economy decreased as the alcohol concentration increased, at a level that was approximately proportionally to the decrease in energy content of the blend. This trend was consistent for both non-FFVs and FFVs, with the E20, Bu32, and E83 blends showing the lowest fuel economies, although lower fuel economy for the E20 and Bu32 fuels was not found for all cycle phases. The Bu55 fuel also showed a higher fuel economy than the E51 fuel.
- PM mass and total particle number emissions were higher for the SIDI vehicles, with the exception of the PFI Ford F-150. Overall, cumulative PM emission results showed reductions with higher oxygen levels for the FFVs over the UC, while E20 showed lower PM emissions than the Bu16 and Bu24 fuels for the non-FFVs. For most vehicles, particle number emissions corroborate the PM mass trends, with the exception of the PFI Ford F-150. Weighted particle number emissions showed lower emissions for the E20 and Bu32 fuels for the non-FFVs, and lower emissions for the higher alcohol blends for the FFVs with E83 showing the lowest emissions. Our results for PM mass emission levels for the SIDI vehicles on the low level ethanol blend (E10) were above or right at the future California LEV III and Tier 3 standards for PM mass emissions to be implemented by 2017 (3 mg/mile), and were clearly above the ultra-low PM standard of 1 mg/mile, which is expected in 2025 in California, indicating that meeting future regulations will require additional PM reductions from the levels observed for current technology

SIDI vehicles.

- Lower molecular-weight aldehydes such as formaldehyde and acetaldehyde were the most abundant carbonyl compounds in the tailpipe for all vehicle/fuel combinations. For the non-FFVs, the fuel blends did not show any statistically significant effect on formaldehyde and acetaldehyde emissions. For the FFVs, acetaldehyde emissions increased significantly for the E51 and E83 fuels. For butyraldehyde, increases were found for Bu16 and Bu32 compared to E20 for the non-FFVs, and for Bu55 compared to the E10, E51, and E83 blends for the FFVs.
- Toluene was the most abundant BTEX, followed by benzene and *m/p*-xylene. For the non-FFVs, benzene and toluene did not show any statistically significant fuel effects, while the Bu32 fuel showed statistically significant reductions in ethylbenzene, *m/p*-xylene, and *o*-xylene relative to different combinations of fuels. For the FFVs, E83 and Bu55 showed lower emissions for the various BTEX species compared to E10 and E51. Emissions of 1,3-butadiene were found at very low concentrations compared to the monoaromatic VOCs. For the FFVs, the Bu55 blend showed a statistically significant increase in 1,3-butadiene compared to E83.

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**APPENDIX**

Table A1. Fuel properties for the ethanol fuel blends

Property	E10	E15	E20	E51	E83	Test Method
Distillation- IBF (°C)	45	43.3	44.4	46.1	48.7	ASTM D86
10 (°C)	58.3	62.2	61.6	63.9	72.5	
50 (°C)	96.6	101.6	72.7	76.1	77.9	
90 (°C)	156.1	153.9	143.9	106.6	78.7	
EP (°C)	173.3	176.6	180	178.3	87	
Specific Gravity	0.7474	0.7474	0.7482	0.770	0.7848	ASTM D4052
Reid Vapor Pressure (kPa)	48.26	47.64	49.64	48.95	42.40	ASTM D5191
Ethanol Content (vol %)	9.96	15.08	20.10	50.89	83.24	ASTM D4815
Total Oxygen (wt %)	3.67	5.56	7.41	18.50	29.68	ASTM D4815
Carbon (wt fraction)	82.54	80.70	78.89	68.28	57.05	ASTM D5291
Hydrogen (wt fraction)	13.85	13.96	13.70	13.43	13.27	ASTM D5291
Sulfur (ppm wt)	10	9	7.56	7	3	ASTM D5353
Aromatics (vol %)	21.8	19.4	19.4	12.7	3.8	ASTM D5580
Multi-substituted aromatics (vol %)	13	13.1	12.0	7.1	2.7	ASTM D5769
Olefins (vol %)	5.1	4.5	4.5	2.3	1	ASTM D6550
RON	92.9	94.6	94.5	105	106	ASTM D2699
MON	84.7	86.1	85.0	89	90.5	ASTM D2700
Octane ((RON+ MON)/2)	88.8	90.4	89.8	97	98.3	ASTM D2699/2700
Net Heat of Combustion (kJ/kg)	41998	40739	39609	34871	28966	ASTM D240

Table A2. Fuel properties for the iso-butanol fuel blends

Property	Bu16	Bu24	Bu32	Bu55	Test Method
Distillation- IBF (°C)	41.6	36.6	43.9	40.5	ASTM D86
10 (°C)	64.4	62.8	61.1	64.9	
50 (°C)	95	98.3	97.2	99.8	
90 (°C)	156.1	158.3	111.1	107.6	
EP (°C)	171.6	192.8	170.5	111.1	
Specific Gravity	0.7535	0.7520	0.7550	0.764	ASTM D4052
Reid Vapor Pressure (kPa)	48.95	47.57	48.95	48.26	ASTM D5191
Iso-Butanol Content (vol %)	15.79	24.01	31.86	53.46	ASTM D4815
Total Oxygen (wt %)	3.58	5.55	7.35	12.16	ASTM D4815
Carbon (wt fraction)	82.79	80.95	79.09	73.61	ASTM D5291
Hydrogen (wt fraction)	13.65	13.66	13.56	14.23	ASTM D5291
Sulfur (ppm wt)	9	8	7	1	ASTM D5353
Aromatics (vol %)	22.8	20.4	17.8	2.5	ASTM D5580
Multi-substituted aromatics (vol %)	13	13	7.2	3.2	ASTM D5769
Olefins (vol %)	5.6	5.1	3.6	1.1	ASTM D6550
RON	93.0	96.9	97.0	99.6	ASTM D2699
MON	84.0	86.2	86.6	87.5	ASTM D2700
Octane ((RON+ MON)/2)	88.5	91.6	91.8	93.6	ASTM D2699/2700
Net Heat of Combustion (kJ/kg)	41023	41049	40330	37944	ASTM D240

Table A3. Fuel properties for the iso-butanol fuel blends

	Honda Civic	Dodge Ram	Toyota Camry	Kia Optima	Chevrolet Impala	Mazda3	Mercedes Benz	Ford F-150	Chevrolet Silverado
Model Year	2007	2007	2012	2012	2012	2012	2012	2013	2014
Displacement, L	1.8	5.7	2.5	2.4	3.6	2.0	3.5	3.7	5.3
Cylinders	Inline, 4 cylinders	V8	Inline, 4 cylinders	Inline, 4 cylinders	V6	Inline, 4 cylinders	V6	V6	V8
Maximum power output, kW	104 at 3600 rpm	257 at 5400 rpm	133 at 6000 rpm	149 at 6300 rpm	224 at 6500 rpm	115 at 6000 rpm	225 at 6500 rpm	225 at 6500 rpm	265 at 5600 rpm
Torque, Nm	173 at 4300 rpm	508 at 4200 rpm	230 at 4100 rpm	252 at 4250 rpm	355 at 5300 rpm	203 at 4000 rpm	370 at 3500-5250 rpm	377 at 4000 rpm	519 at 4100 rpm
Bore x Stroke, mm	81 x 87.3	99.6 x 91	90 x 98	88 x 97	94 x 85.6	83.5 x 91.2	92.9 x 86	94 x 86	96 x 92
Compression ratio	10.5:1	9.6:1	10.4:1	11.3:1	11.5:1	13.0:1	12.0:1	10.5:1	11.0:1
Emissions certification	U.S. Tier 2 Bin 5/ULEV II	U.S. Tier 2 Bin 4/LEV II	U.S. Tier 2 Bin 5/PZEV	Federal Tier 2, Bin 2	LEV II, SULEV	LEV II, SULEV	LEV II, SULEV	LEV II, ULEV	LEV II, ULEV

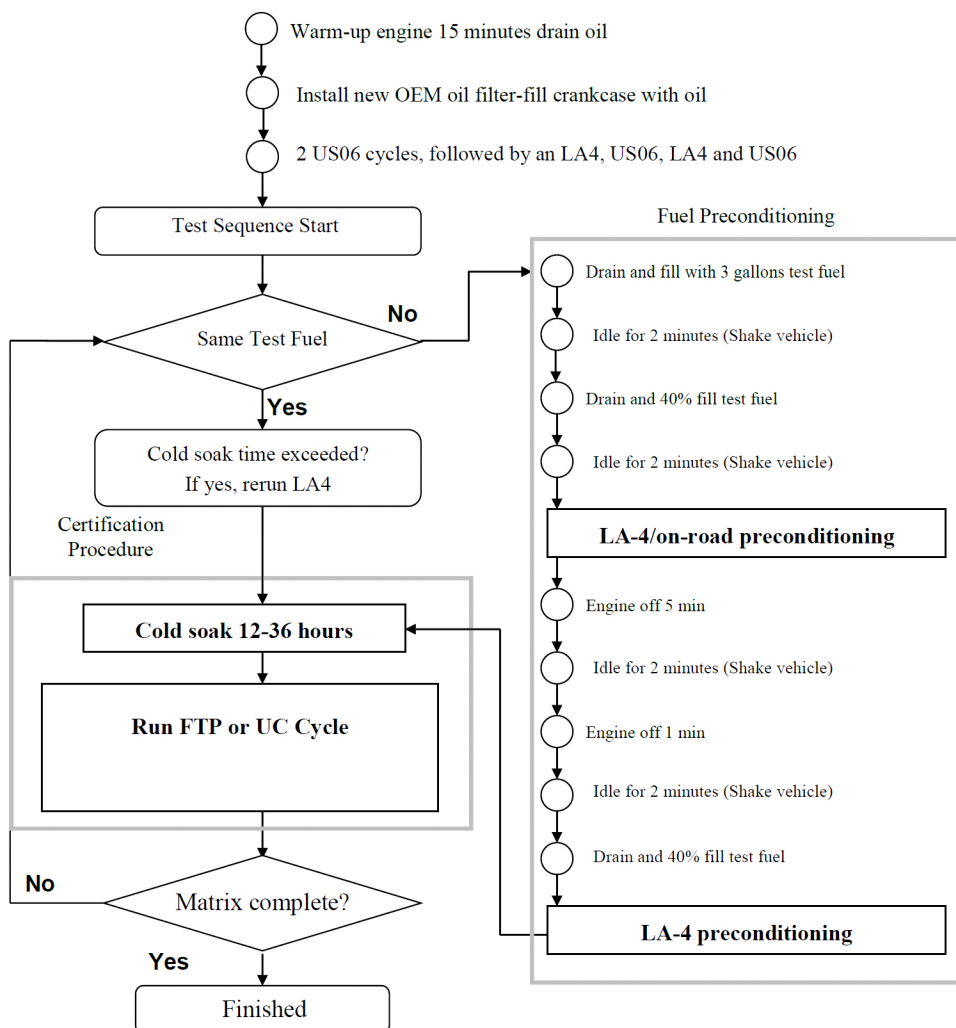


Figure A1. Fuel preconditioning procedure and oil change protocol followed during this study