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# Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends

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## HIGHLIGHTS

- Emissions evaluation from ethanol and iso-butanol GDI and PFI vehicles.
- THC, CO, and $NO_x$ did not show strong trends with ethanol and blends.
- PM mass, number, and black carbon emissions were higher for the GDI vehicles.
- Increasing ethanol and butanol content reduced PM and number emissions.
- Butanol blends enhanced the formation of butyraldehyde emissions.

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## ABSTRACT

This study explores the influence of different mid-level ethanol and iso-butanol blends on the regulated emissions, gaseous air toxics, and particle emissions from three spark ignition port fuel injection (SI-PFI) vehicles and two SI direct injection (DI) vehicles over triplicates Federal Test Procedure (FTP) and Unified Cycles (UC). This study utilized seven fuels with varying ethanol and iso-butanol contents, including E10, E15, E20, Bu16, Bu24, Bu32, and a mixture of E20 and Bu16 resulting in E10/Bu8. Emissions included nitrogen oxides ($NO_x$), carbon monoxide (CO), total hydrocarbons (THC), and carbon dioxide ($CO_2$). Additionally, carbonyl compounds, 1,3-butadiene, benzene, ethylbenzene, toluene, and xylenes were quantified in the exhaust. Particulate matter (PM), total particle number emissions, and black carbon concentrations were also measured. For the regulated emissions, the use of higher ethanol and butanol blends showed some decreases in THC, CO, $NO_x$, and $CO_2$ emissions with the results generally lacking strong trends for the fleet as a whole. Particle mass, number and black carbon emissions were higher for the SI-DI vehicles in comparison with the PFI vehicles, and showed some trends of lower emissions with the use of higher ethanol and butanol blends, with some differences between the fuels being statistically significant. Formaldehyde and acetaldehyde were the most abundant aldehydes in the exhaust, while butyraldehyde showed consistent increases with the butanol blends. The aromatic volatile organic compounds did not show consistent fuel trends.



## 1. Introduction

Globally the on-road transportation sector contributes significantly to air pollution and climate change. One of the challenges for the automotive manufacturers is to decrease pollutant emissions meeting strict fuel economy and carbon dioxide ($CO_2$) emissions requirements. One possible solution is the use of oxygenated biofuels. Biofuels 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 of the demand for fossil fuels. Among the different oxygenated biofuels being used globally today, ethanol is the most widely employed, although geographically its usage is somewhat restricted to U.S. and Brazil. In 2010, the United States (U.S.) Environmental Protection Agency (EPA) implemented the Renewable Fuel Standard (RFS) Program Final Rule, which mandates the use of 36 billion gallons of

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renewable fuels to be blended into transportation fuel by 2022, with ethanol expected to make up the majority of this requirement [1].

Another pathway that could help reach the congressionally mandated biofuel volumes is the use of bio-butanol. Butanol or butyl alcohol also has potential as a biofuel for use in internal combustion (IC) engines [2,3]. Analogous to ethanol, butanol can be produced both by petrochemical and fermentative processes. Biomass-derived butanol can be produced by alcoholic fermentation of biomass and agricultural feedstocks, such as corn, wheat, sugar beet, sugarcane, and cassava [4]. Butanol is a higher-chain alcohol with a four-carbon structure. It exists as different isomers based on the location of the hydroxyl (—OH) group and carbon chain structure. 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 comparison to ethanol, butanol has higher tolerance to water contamination, potentially allowing its use of the existing distribution pipelines, whereas ethanol must be transported via rail or truck [5]. Butanol also has an increased octane number compared to gasoline, but lower than ethanol. Butanol's heat of vaporization is less compared to ethanol, which would provide cold-start benefits for engines running with butanol blended fuels compared with ethanol blends with gasoline [6].

In addition to the alternative fuels diversity in the fuel pool, the automotive manufacturers have taken efforts in improving the overall efficiency of gasoline powered passenger cars, which is directly connected to meeting more stringent carbon dioxide ($CO_2$) emissions limits. To reach $CO_2$ targets, different strategies have been studied, including engine downsizing and higher boost pressures in combination with direct gasoline injection. Direct injection spark ignition (SI-DI) engines can offer up to 25% improvement in fuel economy compared with port-fuel injected (PFI) SI engines [7]. This is mainly achieved through reductions in pumping and heat losses when operated unthrottled at low-mid loads. DI fueling for gasoline engines significantly improves engine power, which allows the engine displacement volume to be reduced for a given application, even while the engine performance improves [8]. The penetration of gasoline DI vehicles in the U.S. market is rapidly increasing. It is foreseen that this category of vehicles will dominate the gasoline market, eventually replacing the conventional and less efficient PFI vehicles. It is interesting to note that in the U.S., half of all light-duty vehicle certifications for the 2012 model year included gasoline DI engines, reaching approximately 24% of the market, up from virtually 0% in 2007. This trend is expected to dramatically increase, with a projection of 48% and 93%, respectively, of all new vehicles having gasoline DI engine by 2016 and 2025 [9].

One of the drawbacks of gasoline DI engines is the increase in particulate emissions in comparison to PFI engines, due to combustion in fuel rich regions in the cylinder. Aakko and Nylund [10] found that particle mass emissions for a gasoline DI vehicle were an order of magnitude higher than for a PFI vehicle for the European 70/220/EEC driving cycle. Szybist et al. [11] reported that particle number emissions with DI fueling increased by 1–2 orders of magnitude compared to PFI fueling. There are also a plethora of studies examining the effects of ethanol on gaseous and particle emissions from SI-PFI and SI-DI vehicles. Studies of older vehicles have generally shown reductions in total hydrocarbons (THC), non-methane hydrocarbon (NMHC), and carbon monoxide (CO) emissions with ethanol blends, while nitrogen oxide ($NO_x$) emissions have either shown no significant changes or increases with increasing ethanol blends [12–14]. Karavalakis et al. [15] found that THC, NMHC, and CO emissions were lower with ethanol blends, while $NO_x$ emissions showed some increases with increasing ethanol content in gasoline. These trends were more consistent for the older 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. A recent study by Bielaczyc et al. [16] 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 particulate matter (PM) mass emissions. Maricq et al. [17] showed small benefits in PM mass and particle number emissions as the ethanol level in gasoline increased from 0% to 20% when they tested a SI-DI turbocharged vehicle with two engine calibrations. They also found higher reductions in both PM mass and particle number emissions with ethanol contents >30%. Finally, Storey et al. [18] reported that $NO_x$ emissions decreased with increased ethanol concentration, while some increases were seen in THC emissions when they tested a turbocharged DI vehicle over the Federal Test Procedure (FTP) cycle and the more aggressive US06 cycle. They also showed reduced PM mass and particle number emissions with ethanol blends.

Butanol has not been studied as extensively as ethanol. An earlier study found that butanol blends resulted in lower $CO_2$, CO, and $NO_x$ emissions compared to gasoline [19]. Dernotte et al. [20] assessed different 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. Schulz and Clark [21] carried out a study comparing various ethanol blends and a 16% 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. With respect to SI-DI engines, Wallner and Frazee [22] found that $NO_x$, CO, and THC emissions were lower with increasing butanol content 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 a similar study, the same authors showed lower volumetric fuel consumption and lower $NO_x$ emissions for butanol compared to ethanol blends [23].

The purpose of this investigation is to elucidate the effects of fuel type and blend concentration for ethanol and iso-butanol on the exhaust emissions from five modern technology light-duty gasoline vehicles fitted with PFI and DI stoichiometric engines. Testing was conducted over the FTP and the Unified Cycle (UC) that include effects of both cold-start and transient operation. The study utilized a total of seven alcohol blends, including 10%, 15%, and 20% ethanol blends and 16%, 24%, and 32% butanol blends, and an alcohol mixture consisting of 20% ethanol and 16% butanol.

## 2. Experimental

### 2.1. Test fuels and vehicles

A total of seven 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 two more ethanol blends, namely E15 and E20. For this study, iso-butanol was blended with gasoline at proportions of 16% (Bu16), 24% (Bu24), and 32% (Bu32) by volume, which is the equivalent of E10, E15, and E20, respectively, based on the oxygen content. In addition, an alcohol mixture consisting of 20% ethanol and 16% iso-butanol (E10/Bu8) was used. This mixed alcohol formulation was equivalent to E15 based on the oxygen content. All fuels were custom blended to match the oxygen contents, maintain the Reid vapor pressure (RVP) within certain limits (6.4–7.2 psi), and match the

fuel volatility properties, except the E10/Bu8 fuel that was a 50/50 splash blend of the E20 and Bu16 fuels. The main physicochemical properties of the test fuels are given in Table S1 in the Supplementary data section.

This study utilized five light-duty gasoline vehicles of different designs (passenger cars and trucks). The vehicles included a 2007 model year (MY) Honda Civic equipped with a PFI engine, a 2007 MY Dodge Ram equipped with a PFI engine, a 2012 MY Toyota Camry equipped with a PFI engine, a 2012 MY Kia Optima equipped with a DI engine, and a 2012 MY Chevrolet Impala equipped with a DI engine. The Honda Civic, Dodge Ram, Toyota Camry, Kia Optima, and Chevrolet Impala had 29,000, 52,400, 13,500, 11,824 and 25,372 miles, respectively, at the start of the test campaign. The technical specifications of the test vehicles are given in Table S2 in the Supplementary data section. 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.

### 2.2. Driving cycles and measurement protocol

Each vehicle was tested on each fuel over three Federal Test Procedure (FTP) and three Unified Cycle (UC) tests. The 6 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. A fuel change with multiple drain and fills was conducted between the testing on each fuel to condition the vehicle and ensure no carryover effects. Detailed information on the driving cycles employed in this study and the testing protocol are provided in Supplementary data section.

### 2.3. 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 schematic on the experimental setup and sampling system on a chassis dynamometer is provided in Fig. S3 in the Supplementary data section. 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, $NO_x$, non-methane hydrocarbons (NMHC), and $CO_2$. NMHC was determined from the combined results from the THC analyzer and a separate $CH_4$ analyzer. Bag measurements were made with a Pierburg AMA-4000 bench. Samples for carbonyl were collected on 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges and analyzed using an Agilent 1200 series high performance liquid chromatograph (HPLC). The HPLC was configured with a diode array detector for the analysis for the PFI vehicles, and was upgraded to a variable wavelength detector for the analyses for the SI-DI vehicles. Samples for 1,3 butadiene, benzene, toluene, ethylbenzene, and xylenes were collected using Carbotrap adsorption tubes and analyzed using an Agilent 6890 GC with a FID. Detailed information regarding the analysis methodology for carbonyl compounds and 1,3 butadiene, benzene, toluene, ethylbenzene, and xylene compounds can be found elsewhere [15].

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, and Chevrolet Impala. The TSI 3772 was replaced by the TSI 3776, since it has a lower cut point, 2.5 nm compared to 10 nm for the TSI 3722, and also a low coincidence error, which is below 300,000 particles per second.

Black carbon measurements were taken with a multi-angle absorption photometer (MAAP). The MAAP is a filter-based measurement that uses one light source at 670 nm to produce photons directed towards the particles accumulated on a Teflocarbon filter paper. The back scattering of these photons is then measured by four photo-detectors located at 45° intervals. As particles accumulate on the filter paper, the light transmitted back or above the filter paper is correlated to the concentration of black carbon, hence the equivalent black carbon mass concentration is reported.

## 3. Results and discussion

The figures for each emissions component show the results for each vehicle tested on the alcohol blends over the FTP and UC cycles based on the average of all tests conducted on that particular fuel blend. The error bars represent the standard deviation for the average of each fuel. Statistical comparisons between fuels for a given vehicle were made using a 2-tailed, 2-sample, equal variance *t*-test. For the purpose of this discussion, results are considered to be statistically significant for $p \leqslant 0.05$.

### 3.1. Regulated emissions

THC emissions for all vehicle/fuel combinations over the FTP and UC test cycles are shown in Fig. 1a. In general, THC emissions were found at low levels for all five vehicles for both test cycles, ranging from 0.005 to 0.12 g/mile for the FTP and 0.005 to 0.09 g/mile for the UC. Higher THC emissions were observed for the older model PFI fueled Honda Civic and Dodge Ram vehicles compared to the newer vehicles. Overall, the largest portion of THC emissions was emitted during the first 200–300 s of the FTP and UC cycles (bag 1) when the engine was cold, ranging from 0.014 to 0.675 g/mile for the FTP and 0.043 to 1.135 g/mile for the UC. The higher cold-start THC emissions can be attributed to the catalyst being below its light-off temperature during the cold-start phase and incomplete combustion products from the fuel enrichment during start up. For the SI-DI vehicles, it was hypothesized that an important source of THC emissions would be fuel impingement on combustion chamber surfaces. It is therefore reasonable to assume that a portion of THC emissions might be derived from unburned fuel fractions during the initial stages of the cold-start portions of the FTP and UC.

Fuel effects showed mixed results for different vehicles and cycles. For the PFI vehicles, the E20 and Bu16 blends showed lower THC emissions for the Honda Civic on the FTP and for the Dodge Ram over the UC, but showed higher THC emissions for the Toyota Camry over the UC. The SI-DI Kia Optima showed some of the strongest trends, with the E15, E20, Bu16, and E10/Bu8 showing higher THC emissions than E10, but the higher butanol blends were either lower or comparable to the Bu16 fuel. The Chevrolet Impala showed very limited fuel differences, with most fuel pairs showing no statistically significant differences.

Trends of decreasing THC emissions with increasing alcohol concentration have generally been seen in previous studies utilizing test cell engines or larger fleets of older technology vehicles [12,15,21,24,25]. 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 [13,20]. The present study did not show strong fuel trends over the fleet

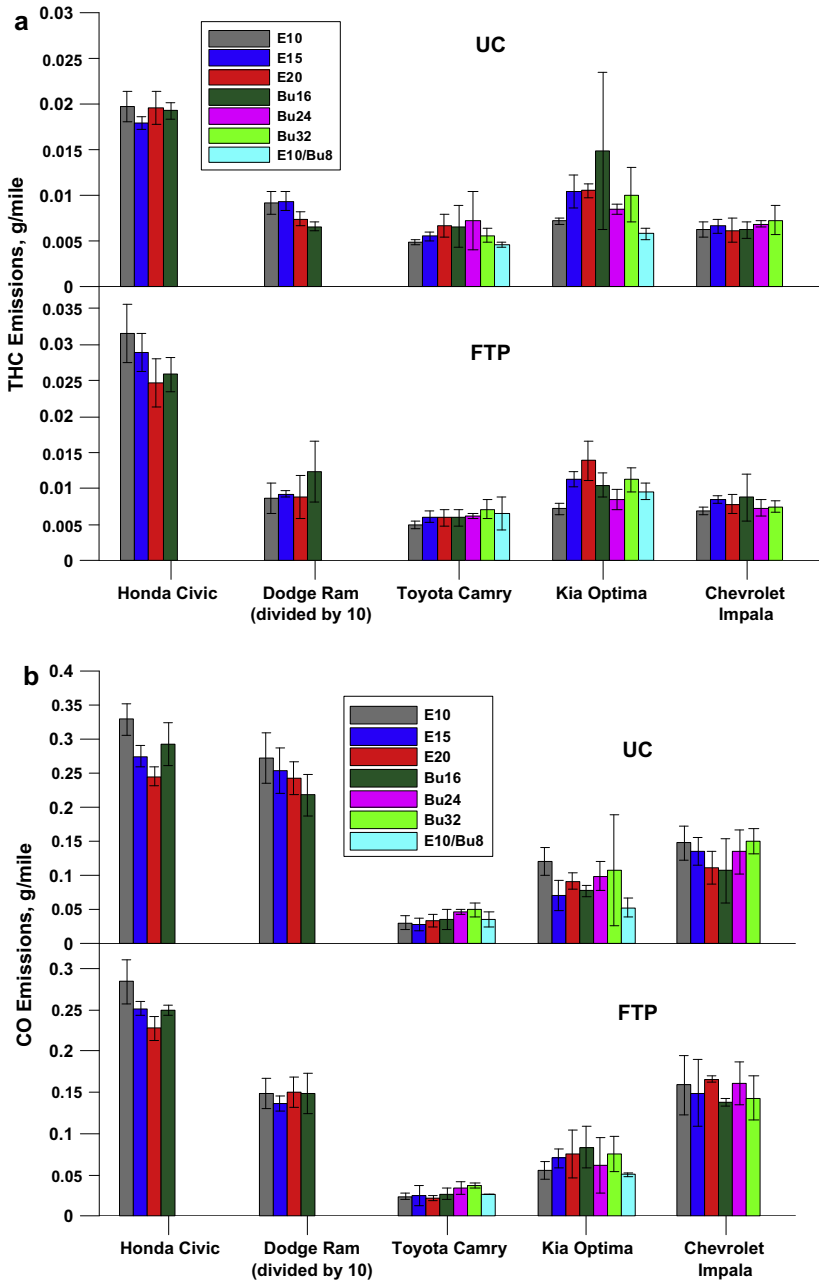


**Fig. 1.** THC (top panel, a) and CO (bottom panel, b) emissions for all vehicle/fuel combinations over the FTP and UC test cycles.

of vehicles tested. In particular, while specific vehicle/cycle combinations may have shown differences between fuels, these differences were generally not consistent for both cycles on a particular vehicle, or for more than one of the vehicles. The lack of strong trends indicates advancements in catalyst technology and air/fuel ratio control are reducing the impact of fuel differences on exhaust emissions. Overall, there is not a strong trend of higher or lower THC emissions for the butanol blends in comparison with the ethanol blends with the equivalent oxygen content. Previous studies have suggested that iso-butanol could produce lower THC emissions due to the lower latent heat of vaporization of iso-butanol compared to ethanol [23].

Fig. 1b presents the influence of ethanol and iso-butanol addition on CO emissions for both cycles. The higher alcohol fuels showed lower CO emissions for the Honda Civic on both cycles and for the higher emitting Dodge Ram over the UC. 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 [15,26]. For the Honda Civic, a statistically significant decrease of 20% for E20 relative to E10 was seen over the FTP, while statistically significant decreases of 17% and 26% for E15 and E20, respectively, relative to E10 were seen over the UC. For the Toyota Camry, CO emissions trended higher with the higher butanol blends, with Bu32 showing a 54% increase in CO emissions compared to E10 at a statistically significant level. For the FTP, the SI-DI vehicles showed no statistically significant differences between the fuels tested. For the UC, the Kia Optima showed some decreases at a statistically significant level in CO emissions with the higher ethanol and butanol blends compared to E10. The Chevrolet Impala showed lower emissions for E20 and Bu16, but not at a statistically significant level. The statistically significant

decreases in CO emissions for the Kia Optima were 41%, 36%, and 56% for E15, Bu16, and E10/Bu8, respectively.

CO production is primarily controlled by the air–fuel ratio in the cylinder. Mixtures richer than stoichiometric produce high CO emissions, whereas mixtures at stoichiometric and leaner produce little CO emissions. For the test fleet as a whole, there were not strong fuel effects on CO emissions, with the exception of some trends of lower CO emissions for higher alcohol blends for the 2007 MY vehicles. This was due to the fact that the test engines utilized stoichiometric combustion and tightly controlled the global equivalence ratio close to 1.0, producing little CO emissions and relatively minor changes in air–fuel ratio throughout testing. The 2007 MY vehicles appear to be more sensitive to small changes in air–fuel ratio, as they produced less CO for the higher alcohol fuel formulations. Analogous to THC emissions, the cold-start portion of the FTP and UC dominated CO emissions for all test vehicles. Comparing the 2012 MY vehicles, the PFI Toyota Camry had relatively low concentrations of CO during the cold-start phase. The relatively low CO suggests that the combustion was not rich. For the SI-DI vehicles, cold-start CO emissions were found to be significantly higher compared to hot-running and hot-start emissions, and considerably higher than those of the Toyota Camry. This result suggests that the combustion was richer for the SI-DI engines during the first 200–300 s of the test cycles. For the 2007 MY PFI vehicles, the CO emissions during cold-start had much high concentrations, while the bags 2 and 3 CO emissions were comparable to those of the newer vehicles. This result implies that these engines run close to stoichiometric and slightly rich through the entire FTP and UC tests.

$NO_x$ emissions as a function of fuel type are shown in Fig. 2. The $NO_x$ emissions for the Honda Civic, Toyota Camry, and the two SI-DI vehicles were about an order of magnitude lower than those for the Dodge Ram. For the Honda Civic, there was a tendency towards higher $NO_x$ emissions over both test cycles for the E15, E20, and Bu16 blends relative to E10. For the FTP, statistically significant increases of 36% and 31%, respectively, for E20 and Bu16 were seen, while for the UC a 54% statistically significant increase in $NO_x$ was observed for E15 relative to E10. For the Dodge Ram, some decreases in $NO_x$ emissions were seen for both cycles, however, these differences were not statistically significant. For the Toyota Camry, lower $NO_x$ emissions were seen for the E15 fuel for the FTP and the Bu24 and Bu32 fuels for both the FTP and UC, but these reductions relative to E10 were only statistically significant for Bu24 (22%) and Bu32 (22%) blends over the UC. For the SI-DI vehicles, $NO_x$ emissions were found to be higher for the Chevrolet Impala than the Kia Optima for the FTP, which trends with the lower THC emissions for the Chevrolet Impala. For the Kia Optima, $NO_x$ emissions did not show any significant differences between the fuels over the FTP, whereas some higher $NO_x$ emissions were seen for E20 (26%) and E10/Bu8 (33%) at a statistically significant level over the UC. For the Chevrolet Impala, the only statistically significant increase in $NO_x$ emissions compared to E10 was seen for Bu32 (29%) blend over the FTP.

$NO_x$ emissions can vary with air–fuel ratio/oxygen content or other combustion factors such as in-cylinder temperatures and the residence time/duration for combustion [27]. Previous studies have shown that $NO_x$ emissions can increase with low, intermediate, and higher ethanol blends, although this trend is not consistent between studies, and is stronger in older vehicles or vehicles with less sophisticated control of air–fuel ratio [12,15,28]. Other studies have shown reductions in $NO_x$ emissions with higher ethanol blends may be due to the higher latent heat of vaporization of ethanol and it's subsequently lower flame temperature, leading to an increase in-cylinder cooling and lower process temperatures, and thus, lower $NO_x$ emissions [24]. Previous investigations have also shown that $NO_x$ emissions can decrease with the addition of butanol [23,29]. Under the present test conditions, there were no consistent fuel trends with oxygenate content, suggesting that individual fuel differences for different vehicles could be related to factors that were unique to the different test vehicles, including test-to-test variability.

Fig. 3a shows the effect of alcohol type and concentration on the $CO_2$ emissions for the test vehicles over the FTP and UC. $CO_2$ emissions showed some specific differences between different fuels for different vehicles, but no consistent trends over all testing conditions. From a theoretical standpoint, it might be expected that $CO_2$ emissions would trend with either the carbon/hydrogen ratio or carbon/energy content in the fuel. Carbon/hydrogen ratio

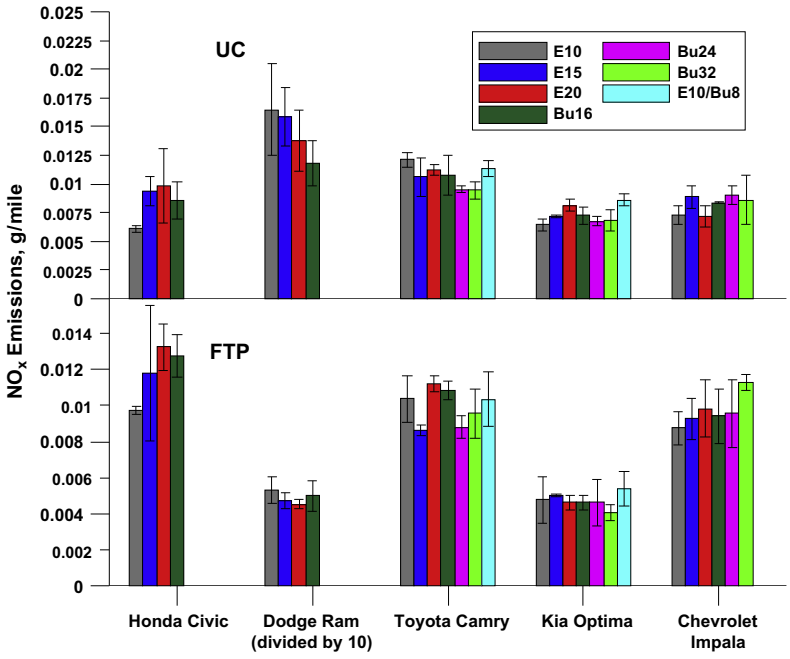


**Fig. 2.** $NO_x$ emissions for all vehicle/fuel combinations over the FTP (bottom panel) and UC (top panel) test cycles.

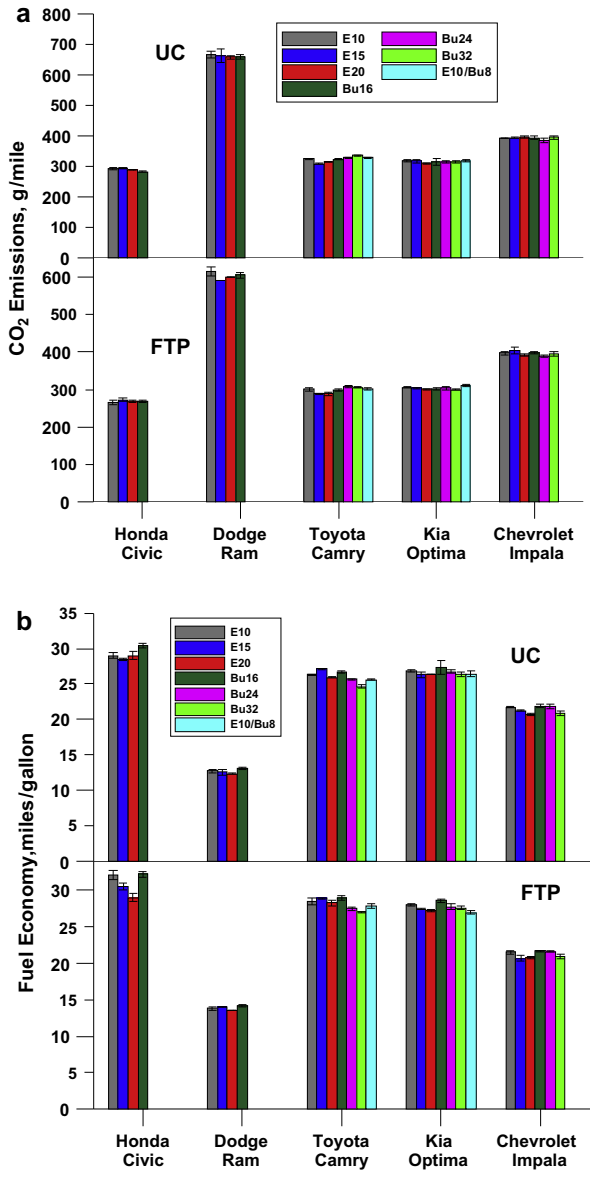


**Fig. 3.** $CO_2$ (top panel, a) emissions and fuel economy based on the carbon balance method (bottom panel, b) for all vehicle/fuel combinations over the FTP and UC test cycles.

decreases in the following order E10–Bu16, E15–Bu24–E10/Bu8, and E20–Bu32, as shown in Table S1 of the Supplementary data section. Overall, there are not universal trends relating to either of these metrics, but in the cases where fuel differences are seen for the different vehicles, they tend to track better with the decreasing carbon/hydrogen ratio. Reductions in $CO_2$ emissions at a statistically significant level for the lower carbon/hydrogen ratio fuels were seen for the Dodge Ram over the FTP, but not for the UC, and the Toyota Camry for both the FTP and UC cycles, but not for the butanol blends. Interestingly, the Honda Civic over the UC did show a trend of lower $CO_2$ emissions for the E15 and E20 blends relative to the E10 fuel, but higher $CO_2$ emissions relative to the Bu16 fuel. The SI-DI vehicles exhibited lower $CO_2$ emissions for the higher ethanol blends with some differences being statistically significant for the Kia Optima. For the Chevrolet Impala, $CO_2$ emissions were about the same between the fuels over both test cycles, with some weak trends towards lower $CO_2$ emissions for the higher ethanol and butanol blends relative to E10.

Fuel economy results for the test vehicles are presented in Fig. 3b. For this study, 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. Overall, the results revealed that as the alcohol concentration increased the fuel economy decreased by 2–5% for the FTP and 1–6% for the UC, which is approximately proportionally to the decrease in energy content of the blend. This trend was consistent for all vehicles, with the higher ethanol blends and butanol blends showing lower fuel economy than E10 and Bu16, respectively, while the E10/Bu8 blend had about the same fuel economy as the E15 blend for the SI-SIDI vehicles and a slightly lower fuel economy for the Toyota Camry.

### 3.2. PM mass, particle number, and black carbon emissions

The cumulative PM mass emissions are shown in Fig. 4a. Note that PM mass was only collected for the SI-DI vehicles and for most of the fuels for the Toyota Camry. PM mass emission results for the SI-DI vehicles showed reductions with the fuels with the highest

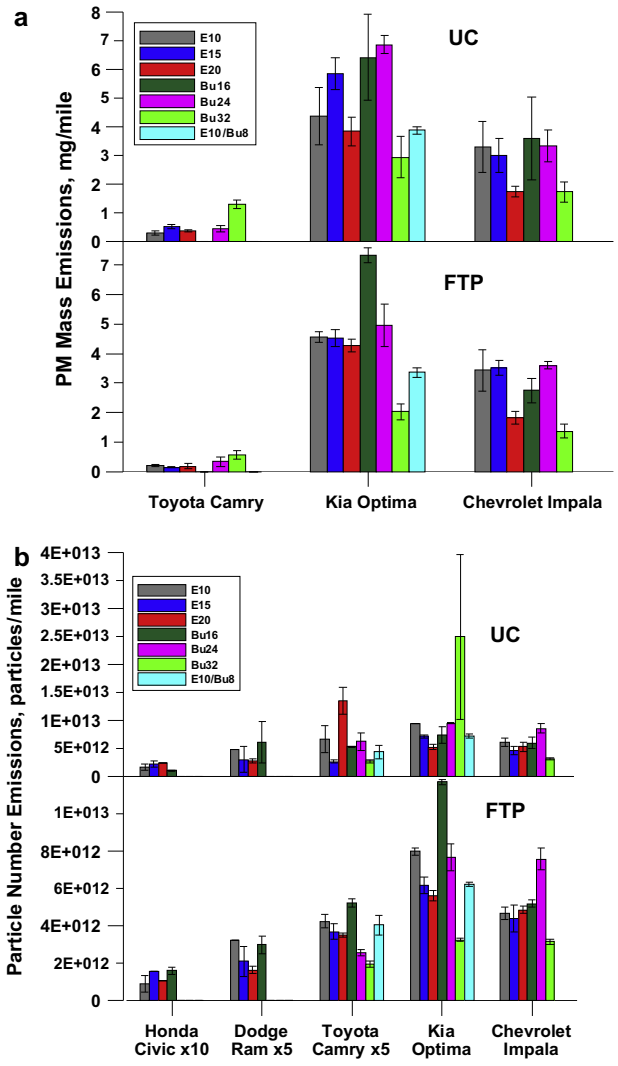


**Fig. 4.** PM mass emissions for the Toyota Camry and the SI-DI vehicles over the FTP and UC test cycles (top panel, a) and total particle number emissions for all vehicle/fuel combinations over the FTP and UC test cycles (bottom panel, b).

oxygen levels for a number of the vehicle/cycle combinations, but not necessarily the blends with the intermediate oxygen levels. Other properties, such as fuel volatility, can also play a role in PM emissions, which is sometimes more important than the presence of oxygen in the fuel. However, in the current study most physicochemical properties of the test fuels were kept constant with relatively narrow ranges. Thus, the oxygen content should be the primary contributing factor for lowering PM emissions.

For the Chevrolet Impala, the PM mass results showed some trends with the oxygen content in the fuel, with the E20 and Bu32 fuels showing the lowest PM mass levels over both cycles. For the butanol blends for the Chevrolet Impala, PM benefits were seen for the higher butanol fuels relative to Bu16 over the UC and for Bu32 compared to both Bu16 and Bu24 over the FTP. For the Kia Optima, the E20 and Bu32 fuels showed the lowest PM mass emissions for both the FTP and UC cycles. For the Kia Optima, the Bu32 fuel showed the lowest PM mass emissions, while the Bu16 showed the highest emissions over the FTP. Over the UC for the Kia Optima, the fuel trends were less consistent, with the E15, Bu16, and Bu24 fuels showed the highest emissions, while the Bu32 fuel was slightly lower than the remaining fuels. For the Toyota Camry, the use of higher ethanol blends produced discordant results with both decreases in PM emissions over the FTP and increases over the UC. While the reductions in PM emissions for the FTP were not statistically significant, the use of E15 led to a statistically significant 74% increase in PM emissions relative to E10 over the UC. For both test cycles, the use of higher butanol blends resulted in increases in PM emissions compared to ethanol blends, although data on Bu16 and E10/Bu8 is missing to draw a more complete picture of how the ethanol and butanol blends compare. The Bu32 blend showed dramatic increases in PM emissions relative to E10 at a statistically significant level on the order of 183% and 336% for the FTP and UC, respectively.

PM mass results ranged from 0.15 to 7.3 mg/mile for the FTP and 0.30 to 6.87 for the UC, averaging 0.28 and 0.59 mg/mile for the Toyota Camry, 4.40 and 4.88 mg/mile for the Kia Optima, and at 2.75 and 2.78 mg/mile for the Chevrolet Impala for the FTP and UC, respectively. This study showed considerably higher PM mass emissions from the SI-DI vehicles compared to the PFI vehicle. High PM emissions for the SI-DI fueled vehicles are expected and have been reported in previous studies [30,31]. 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 [32]. Elevated PM mass emissions from SI-DI vehicles can be ascribed to insufficient homogeneous mixture 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 [33,34]. In addition, the higher PM emissions from the SI-DI 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 [31]. It should be noted that while this study employed relatively modern SI-DI vehicles, these vehicles did not have sufficient control of PM emissions meet the future California LEV III and Tier 3 standards for PM mass emissions to be implemented in 2017 (3 mg/mile), and in particular the even more stringent LEV III PM mass standards for 2025 (1 mg/mile).

The total particle number emissions are displayed in Fig. 4b. For the SI-DI vehicles, particle number emissions corroborate the PM mass trends, with the Kia Optima generally showing higher particle number emissions than the Chevrolet Impala. Both SI-DI vehicles exhibited significantly higher particle number counts compared to their PFI counterparts. This can be ascribed to the better mixture preparation of PFI engines in relation to SI-DI engines and the likelihood of fuel impingement onto the piston for the SI-DI 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 [35,36]. Overall, the more aggressive driving conditions for the UC increased particle number counts for all vehicle/fuel combinations compared to the FTP.

For the FTP, the use of E15 and E20 reduced particle number emissions compared to E10, with some exceptions. For the UC, the use of E15 and E20 blends showed mixed results with some particle number benefits for the Dodge Ram and the Kia Optima. For the Kia Optima, the blends of E15 and E20 exhibited statistically significant decreases in particle number emissions of 23% and 30%, respectively, compared to E10. Particle number for E15 and E20 benefits were also seen over the UC, however, no statistical comparisons can be made due to the fact that only a single test was available for E10 for the UC. For the Chevrolet Impala, particle number emissions for E10, E15, and E20 were not significantly different for both cycles. For the butanol blends, particle number comparisons were complicated for some vehicles and some butanol blends. For the 2007 PFI vehicles, the use of Bu16 increased particle number emissions compared to E15 and E20 for both cycles, except for the Honda Civic over the UC. For the Toyota Camry, particle number emissions for Bu16 remained roughly the same as those of E10 for both cycles, while lower particle number emissions were observed for the higher butanol blends compared to Bu16 with these reductions over the FTP being statistically significant. For both cycles, the E10/Bu8 blend was at about the same levels as the E15. Analogous to ethanol blends, the Kia Optima showed statistically significant decreases in particle number emissions for the FTP were also seen for Bu24 (34%) and Bu32 (72%) blends relative to Bu16. The alcohol mixture (E10/Bu8) showed a statistically significant reduction in particle number emissions from both E10 (22%) and Bu16 (47%) blends, respectively. For the UC, however, a different picture was observed for the butanol blends. The higher butanol blends resulted in increases in particle number emissions compared to Bu16 with Bu32 showing a sharp increase of 236% at a statistically significant level. For the butanol blends for the Chevrolet Impala, there was 46% and 44% increase in particle number emissions for Bu24 relative to Bu16 at a statistically significant level over the FTP and UC, respectively. Statistically significant decreases of 39% and 47%, respectively, for the FTP and UC for Bu32 compared to Bu16 were also observed.

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. In addition to the oxygen content, particles are also strongly related to the aromatic hydrocarbons content in the fuel [25]. 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. This is consistent with the findings of Wallner and Frazee [22], 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. The iso-butanol blends had higher particle number emissions compared to their corresponding ethanol blends in some cases, but not in others, although the Bu32 blend emitted the lowest particle number emissions for most vehicle/fuel combinations. Previous studies have suggested that during SI-DI combustion branched butanols can produce intermediate products, such as propene and butene, leading to the formation of more benzene and soot [37]. The results of this study indicate that, in some cases, the degree of branching (iso-butanol versus ethanol) may have a stronger impact on soot formation than the oxygen content, since the 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 have also influenced particle number emissions by altering the fuel spray characteristics [38].

The cold-start phase for both test cycles contributes strongly to the overall particle number emissions, as the engine and catalyst are not yet at operating temperature and therefore particles consisting of volatile residues cannot be effectively oxidized. It is interesting to note that most of the particle emissions occur towards the beginning of the FTP and UC, with roughly 60–90% of the particle emissions occurring in the first 200–300 s. More specifically, for the Honda Civic, fuel average particle number counts for cold-start, hot-running emissions, and hot-start were $3.46 \times 10^{11}$, $9.14 \times 10^{10}$, and $4.62 \times 10^{10}$ #/mile for the FTP and $9.52 \times 10^{11}$, $1.42 \times 10^{11}$, and $9.67 \times 10^{10}$ #/mile for the UC, respectively. For the Dodge Ram, fuel average particle number counts were $1.48 \times 10^{12}$, $2.52 \times 10^{11}$, and $2.40 \times 10^{11}$ #/mile for the FTP and $2.59 \times 10^{12}$, $6.77 \times 10^{11}$, and $3.01 \times 10^{11}$, #/mile for the UC, respectively. For the Toyota Camry fuel average particle number counts were $1.75 \times 10^{11}$, $2.58 \times 10^{10}$, and $3.26 \times 10^{10}$ #/mile for the FTP and $1.58 \times 10^{12}$, $1.19 \times 10^{11}$, and $3.10 \times 10^{10}$ #/mile for the UC, respectively. For the Kia Optima, fuel average particle number counts were $1.95 \times 10^{13}$, $3.82 \times 10^{12}$, and $2.64 \times 10^{12}$ #/mile for the FTP and $4.44 \times 10^{13}$, $8.72 \times 10^{12}$, and $3.57 \times 10^{12}$ #/mile for the UC, respectively. Finally, for the Chevrolet Impala, fuel average particle number counts were $1.91 \times 10^{13}$, $1.39 \times 10^{12}$, and $9.40 \times 10^{11}$ #/mile for the FTP and $4.60 \times 10^{13}$, $3.50 \times 10^{12}$, and $1.09 \times 10^{12}$ #/mile for the UC, respectively. The cold-start emissions for the UC are substantially higher compared to those of the FTP, because the cold-start phase for the FTP is about ~200 s longer than that for the UC, and hence includes some driving after the initial spike in cold-start emissions has ended. For the UC, hot-running particle emissions were also systematically lower than those for the hot-start due to the driving schedule being less aggressive than in the hot-running phase and that there is a much lower tendency to overfuel in the hot-start compared with the cold-start. For the cold-start for the SI-DI vehicles, fuel accumulation onto the cold piston and cylinder surfaces can contribute to the sharp increases in particle number emissions. Hot-running and hot-start particle emissions for the FTP did not show significant differences as opposed to those of the UC. The significant reduction in particle number emissions after the cold-start can be attributed to the higher intake air temperatures, fuel temperatures, and piston surface temperatures, which promote fuel vaporization and thus better fuel–air mixing, coupled with the higher efficiency of the TWC once it has reached its light-off temperature [34].

Fig. 5 shows the black carbon concentrations, expressed in μg/m$^3$, for all vehicle/fuel combinations over the FTP and UC. It should be mentioned that the MAAP was not available for Bu32 for the Kia Optima and for Bu16 and Bu24 for the Chevrolet Impala. Black carbon is generally formed through incomplete combustion and it has recently become a higher priority to regulatory and environmental agencies due to its global warming potential in addition to the known greenhouse gases. Besides its direct influence on the climate, black carbon also adversely effects visibility, human health, and act as a cloud condensation nuclei [39]. Overall, the black carbon results were mixed and did not follow a uniform trend for both test cycles. Clearly, black carbon emissions were 3–7 times higher for the SI-DI vehicles compared to PFI vehicles, suggesting that SI-DI PM were primarily elemental carbon or soot in nature. This does not apply to PFI vehicles where the PM is primarily organic in nature [17]. For the FTP, black carbon reductions with increasing alcohol concentration were seen for the Dodge Ram, Toyota Camry, and Chevrolet Impala. For the UC, some reductions in black carbon emissions were seen for the Toyota Camry, with the Dodge Ram showing increases in black carbon with the higher alcohol fuels,

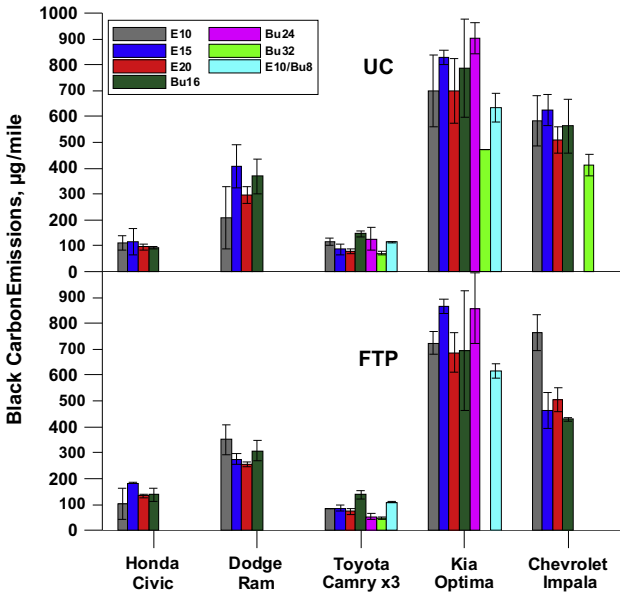


**Fig. 5.** Black carbon concentrations for all vehicle/fuel combinations over the FTP (bottom panel) and UC (top panel) test cycles.

and the Kia Optima and the Chevrolet Impala showing insignificant differences. The reductions in black carbon emissions could be attributed to the higher oxygen content in the fuel, which can reduce the tendency to form soot. A relatively good correlation was found for black carbon and particle number emissions for the PFI vehicles, especially for the FTP, although the correlation was not strong for the UC or the SI-DI vehicles. It is also interesting to note that most of the black carbon emissions occurred during the cold-start phases of the FTP and UC, due to the reduced fuel vaporization and wall impingement, and the reduced efficiency of the TWC. These findings are in agreement with those of a recent chassis dynamometer study on light-duty gasoline vehicles [40].

### 3.3. Carbonyl emissions

Carbonyl compounds are displaying in Figs. 6 and 7 for the PFI-fueled vehicles and DI-fueled vehicles, respectively. Carbonyl emissions were only measured over the FTP. 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, benzeldehyde, propionaldehyde, crotonaldehyde, and methacrolein. For the SI-DI vehicles, a more sensitive detector was utilized for the carbonyl analysis, so other carbonyl compounds were also identified, albeit in lesser amounts, including those of MEK, valeraldehyde, and hexanaldehyde. Hexanaldehyde was detected in small concentrations for some fuel blends, and generally decreased by the addition of oxygenates in gasoline. The aromatic tolualdehyde was undetectable for all fuel blends and for both test vehicles.

Total carbonyl emissions showed mixed results from vehicle to vehicle and between different fuels. Total carbonyls for E15 (1.669 ± 0.475 mg/mile) and E20 (3.440 ± 0.426 mg/mile), respectively, for the Honda Civic and the Dodger Ram showed the highest emissions compared to E10 (0.889 ± 0.178 and 1.855 ± 0.464 mg/mile for the Honda Civic and the Dodge Ram, respectively) as well as other fuels. For the Toyota Camry, on the other hand, the differences in total carbonyls for the ethanol and butanol blends were small. For the Kia Optima, total carbonyls for Bu16 (0.742 ± 0.341), Bu24 (1.040 ± 0.772), and E10/Bu8 (1.429 ±

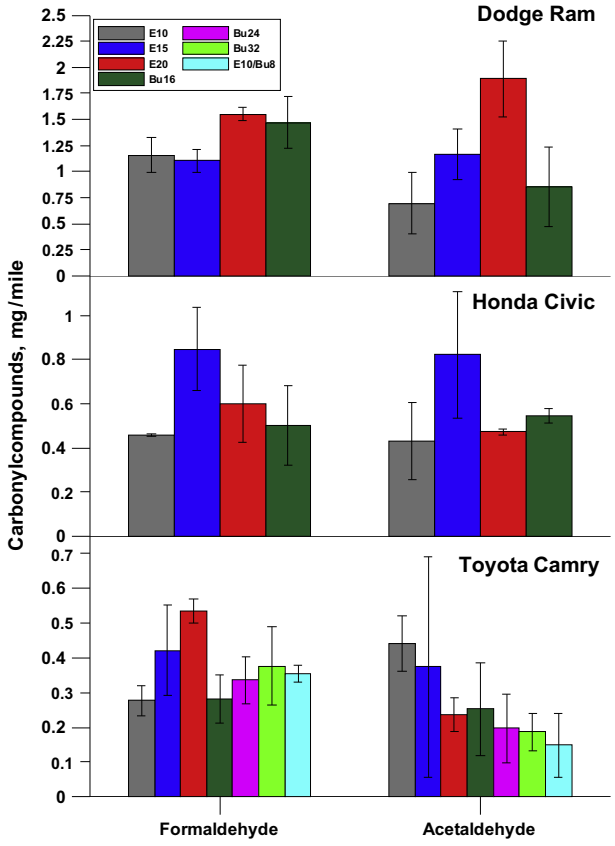


**Fig. 6.** Carbonyl emissions for the PFI-fueled vehicles over the FTP test cycle.

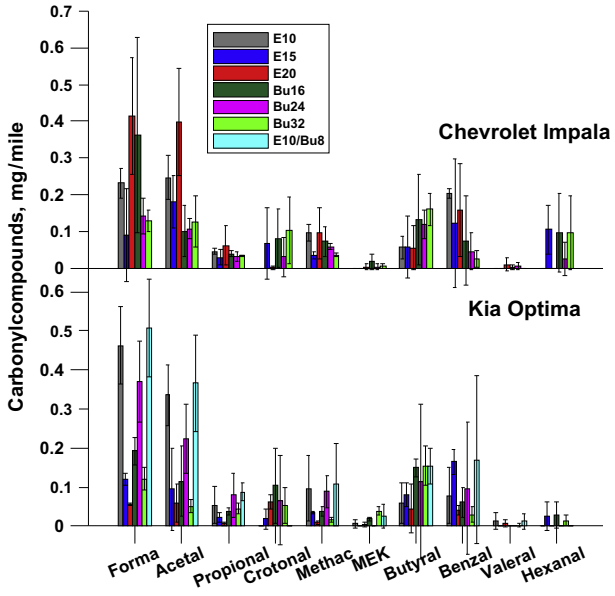


**Fig. 7.** Carbonyl emissions for the SI-DI vehicles over the FTP test cycle.

0.685) were higher than those measured for E15 (0.561 ± 0.261) and E20 (0.287 ± 0.168). Finally, for the Chevrolet Impala, total carbonyls did not show strong fuel trends.

For the PFI-fueled vehicles, formaldehyde showed some increases with E15 and E20 relative to E10, while Bu16 had roughly the same levels of formaldehyde emissions as E10. For the Toyota Camry, formaldehyde emissions for the different butanol blends were comparable within the experimental variability. Acetaldehyde emissions exhibited some increases with E15 and E20 for the Honda Civic and Dodge Ram, but not for the Toyota Camry. For the Toyota Camry, statistically significant decreases in acetaldehyde emissions were seen for E20, Bu24, Bu32, and E10/Bu8 relative to E10. For both SI-DI vehicles, a clear reduction in formaldehyde and acetaldehyde emissions was observed for E15 relative to E10. For the Chevrolet Impala, an increase in both formaldehyde and acetaldehyde emissions was also seen for E20 relative to E10 blend, but not at a statistically significant level. On the contrary, for the Kia Optima, E15 and E20 blends showed marked and statistically significant reductions in both formaldehyde and acetaldehyde emissions relative to E10. For formaldehyde, these reductions were 74% and 88% for E15 and E20, respectively, while for acetaldehyde the reductions were 72% and 82% for E15 and E20, respectively. For the Kia Optima, the use of Bu24 resulted in higher formaldehyde and acetaldehyde emissions than Bu16 and both E15 and E20 blends, while Bu32 blend clearly led to decreases in formaldehyde and acetaldehyde emissions compared to Bu16. The alcohol mixture E10/Bu8 exhibited similar formaldehyde and acetaldehyde emission levels with the E10 blend. For the Chevrolet Impala, the higher butanol blends showed some decreases in formaldehyde and acetaldehyde emissions compared to Bu16, but not at a statistically significant level.

Generally, gasoline fuels do not contain carbonyl compounds with the emissions of aldehydes and ketones being a result of partial oxidation of the fuel components during combustion. Previous studies have shown that the addition of ethanol and butanol fuels can produce higher formaldehyde and acetaldehyde emissions [15,22,26,41]. Formaldehyde is produced from oxygenated fuels and also by decreasing of fuel aromatics, since aromatics do not participate in the formation of formaldehyde [42]. For the butanol blends, formaldehyde can be produced from simple fission followed by $\beta$-scission, which produces both an alkane and the aldehyde. Acetaldehyde is principally produced through the partial oxidation of ethanol. In the case of butanol fuels, acetaldehyde can also be formed via $\beta$-scission of a$C_4H_8OH$ [43]. McEnally and Pfefferle [37] 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. [44] 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 SI-DI vehicles.

Butyraldehyde emissions appeared to be higher with the use of higher iso-butanol blends. This finding is in agreement with a recent chassis dynamometer study, which showed higher butyraldehyde emissions for butanol fuels [45]. For both SI-DI vehicles, the butanol blends and the E10/Bu8 mixture showed higher butyraldehyde emissions than the ethanol blends. It is assumed that butyraldehyde was formed via H-atom abstraction of one of the decomposition products of iso-butanol. The increased butyraldehyde emissions for the higher butanol blends could be an important finding because it possesses similar reactivity and mutagenicity properties than acetaldehyde [46]. Benzaldehyde, which is primarily produced from fuel aromatic hydrocarbons, showed mixed trends with the alcohol fuels for the SI-DI vehicles, with the Kia Optima produced both increases and decreases in benzaldehyde emissions with the higher ethanol and butanol blends but not at statistically significant level. For the Chevrolet Impala, benzaldehyde emissions showed some lower emissions with the higher ethanol and butanol blends compared to E10 and Bu16, respectively, although these differences were not statistically significant due to the experimental variability. Our results are in agreement with those studies showing that the addition of oxygenates decreases benzaldehyde emissions [15,18,26], but also

consistent with other studies showing some increases in benzaldehyde emissions probably because of the enhancement of aromatics oxidation [42,47]. We hypothesized that benzaldehyde can be produced from oxygen addition to different types of aromatics, including alkyl branches of toluene, xylene, and trimethylbenzene present in gasoline. Methacrolein emissions trended lower with higher ethanol and butanol blends with some exceptions, indicating that neither ethanol nor butanol participating in the formation of this pollutant.

Carbonyl emissions were also influenced by the driving cycle and the cold-start phase of the FTP. In general, carbonyls were found to be higher during the cold-start phase and slightly higher during the hot-running phase of the FTP compared to phase 3. The fuel average total carbonyls were 3.45, 0.65, and 0.33 mg/mile for the Honda Civic, 8.13, 1.03, and 0.81 mg/mile for the Dodge Ram, and 1.37, 0.46, and 0.33 mg/mile for the Toyota Camry for the cold-start, hot-running, and hot-start phases of the FTP, respectively. For the SI-DI vehicles, the fuel average total carbonyls were 2.34, 1.00, and 0.62 mg/mile for the Kia Optima and 2.05, 0.88, and 0.84 mg/mile for the Chevrolet Impala for the cold-start, hot-running, and hot-start phases of the FTP, respectively. These observations indicate that the higher cold-start emissions are mainly related to catalyst inactivity, while the lower total carbonyls for phases 2 and 3 were due to the increased exhaust temperatures and the higher efficiency of the TWC, which facilitates the oxidation of aldehyde species.

### 3.4. Volatile organic compounds

Figs. 8 and 9 present the cumulative 1,3-butadiene, benzene, ethylbenzene, toluene, *m/p*-xylene, and *o*-xylene for the PFI and DI vehicles, respectively, over the FTP. These pollutants were only measured for the FTP cycle. The aromatic hydrocarbons of benzene, ethylbenzene, toluene, *m/p*-xylene, and *o*-xylene are commonly termed to as BTEX. The most reactive volatile organic compounds (VOCs) from internal combustion engines are BTEX compounds, since they contain a C=C bond, that can add free radicals. It is evident that toluene was the most abundant VOC, followed by *m/p*-xylene and benzene. For benzene emissions, whose principal source is partial combustion of toluene and xylene, some decreasing trends were seen for the Honda Civic and the Dodge Ram with the higher alcohol blends but not at a statistically significant level. Interestingly, for the Toyota Camry, the use of higher ethanol and butanol blends resulted in higher benzene emissions relative to E10 with E20 and Bu32 showing statistically significant increases of 32% and 36%, respectively, compared to E10. For the SI-DI vehicles, some increases in benzene emissions were observed for certain higher alcohol blends compared to E10. For the Kia Optima, statistically significant increases of 112% and 91%, respectively, for E20 and Bu16 relative to E10 were observed. For the Chevrolet Impala, the only statistically significant increase in benzene emissions relative to E10 was for Bu24 (111%). Toluene did not show any strong fuel effects for the Honda Civic and the Dodge Ram, while for the Toyota Camry exhibited some decreases with the higher ethanol blends compared to E10 and the higher butanol blends compared to Bu16. Toluene emissions trended higher with increasing alcohol concentration for the SI-DI vehicles, with Bu24 showing a statistical significant increase of 45% relative to E10 for the Chevrolet Impala, and E15, E20, and Bu16 was showing statistically significant increases of 148%, 136%, and 127%, respectively, for the Kia Optima. Ethylbenzene emissions did not exhibit any significant differences between fuels for the PFI vehicles, with the exception of the Toyota Camry, where higher ethylbenzene emissions were observed for the E10/Bu8 (33%) mixture relative to E10 at a statistically significant level. Statistically significant increases in ethylbenzene emissions were also seen for E20

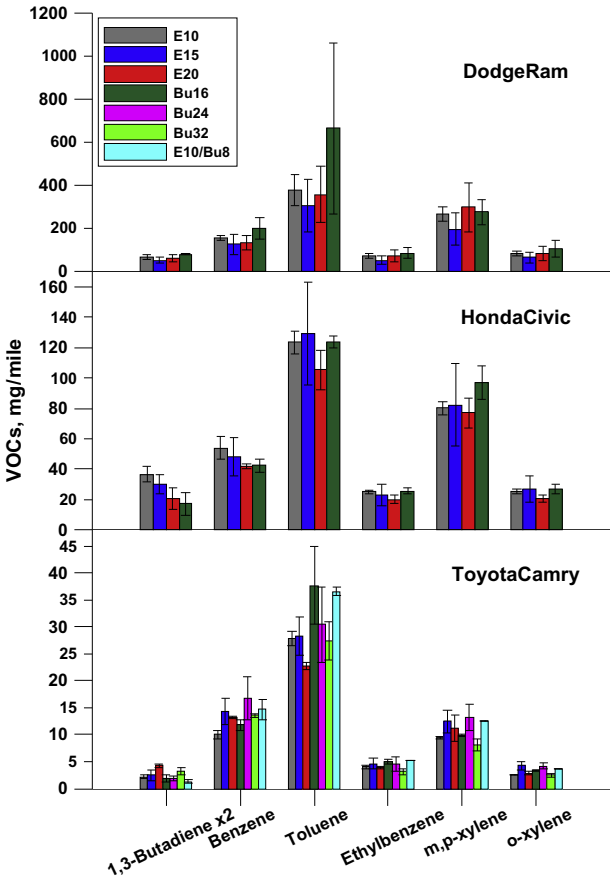


**Fig. 8.** BTEX emissions and 1,3-butadiene for the PFI-fueled vehicles over the FTP test cycle.

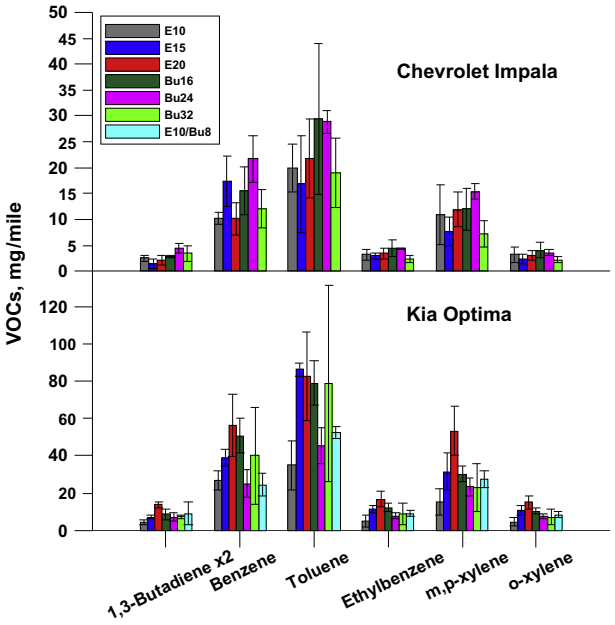


**Fig. 9.** BTEX emissions and 1,3-butadiene for the SI-DI vehicles over the FTP test cycle.

(264%) and Bu16 (159%) relative to E10 for the Kia Optima. For the Chevrolet Impala, no statistically significant differences were seen between the fuels for ethylbenzene emissions. Xylenes

showed rather minor differences between the fuels for the PFI vehicles, with the Toyota Camry showing some statistically significant increases in xylene emissions compared to E10 for some fuels. While xylene emission levels were about the same for different fuels for the Chevrolet Impala, for the Kia Optima xylene emissions were higher at a statistically significant level for E20 and Bu16 relative to E10.

Emissions of 1,3-butadiene were generally found at very low concentrations for all vehicle/fuel combinations compared to the aromatic VOCs. For the Honda Civic, 1,3-butadiene emissions were lower for E15, E20, and Bu16 compared to E10, with Bu16 showing a statistically significant reduction of 52% relative to E10. No particularly strong trends were seen for the Dodge Ram and the Toyota Camry in 1,3-butadiene emissions, with the exception of E20 for the Toyota Camry, which showed a statistically significant increase in 1,3-butadiene of 94% relative to E10. For the Kia Optima, 1,3-butadiene emissions for the butanol blends were roughly the same, while some increases were found for the higher ethanol blends compared to E10, with E20 exhibiting a statistically significant increase in 1,3-butadiene emissions of 199% compared to E10. For the Chevrolet Impala, 1,3-butadiene emissions were higher at a statistically significant level for Bu24 blend compared to both E10 and Bu16. Overall, aromatic VOCs exhibited varied results over the different test conditions, but some increases for different ethanol/butanol blends for the SI-DI vehicles. Given the widespread penetration of both alcohol fuel formulations and SI-DI vehicles, the results suggest that there is a need for more extensive speciated emissions measurements for these fuels on SI-DI engines due to the fact that VOCs react photochemically in the atmosphere to form secondary PM in the form of secondary organic aerosols (SOA).

## 4. 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, seven alcohol formulations including ethanol blends, iso-butanol blends and an alcohol mixture were tested on five different light-duty vehicles. Testing was performed on three SI-PFI vehicles and two wall-guided SI-DI vehicles over the FTP and UC test cycles using a light-duty chassis dynamometer.

For THC, CO, and $NO_x$ emissions, the results did not show strong fuel trends. Although some fuel differences were identified, these differences were generally not consistent for both cycles on a particular vehicle, or for more than one of the vehicles. The lack of strong trends indicates advancements in catalyst technology and air/fuel ratio control are reducing the impact of fuel differences on exhaust emissions. Our results also indicated that THC, CO, and $NO_x$ emissions were predominantly obtained during the cold-start phase, when the catalyst was temporarily cold and inactive. $CO_2$ emissions showed reductions in some cases for the higher alcohol blends, while fuel economy based on the carbon balance method showed decreases with increasing alcohol concentration in the fuel. PM mass was substantially lower for the PFI vehicles compared to the SI-DI vehicles. PM mass emission results for the SI-DI vehicles showed reductions with the fuels with the highest oxygen levels for a number of the vehicle/cycle combinations, but not necessarily the blends with the intermediate oxygen levels. Analogous to PM mass, particle number emissions were significantly lower for the PFI-fueled vehicles compared to the SI-DI vehicles. In general, particle number emissions showed reductions with increasing ethanol and butanol concentration in the fuel, with these differences being statistically significant for some fuels and some vehicles but not for others. Black carbon results showed higher emissions for the SI-DI vehicles than the PFI vehicles, and showed lower emissions for the higher alcohol blends for a limited number of vehicle/cycle combinations.

Formaldehyde and acetaldehyde were the most abundant aldehydes in the exhaust for all fuel/vehicle combinations, with heavier aldehydes being also present, but in lesser amounts. For the PFI vehicles, formaldehyde and acetaldehyde showed some increases for the higher ethanol blends, but these trends were not consistent. For the SI-DI vehicles, both increases and decreases were seen with the higher ethanol and butanol blends compared to E10 and Bu16. It was found that the use of butanol blends enhanced the formation of butyraldehyde emissions, which is considered a reactive and mutagenic aldehyde compound. Emissions of 1,3-butadiene and aromatic VOCs did not follow a global trend between the fuels and vehicles tested.

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## Appendix A. Supplementary materials

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2014.03.016.

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