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# Assessing the Impacts of Ethanol and Isobutanol on Gaseous and Particulate Emissions from Flexible Fuel Vehicles

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**S** *Supporting Information*

**ABSTRACT:** This study investigated the effects of higher ethanol blends and an isobutanol blend on the criteria emissions, fuel economy, gaseous toxic pollutants, and particulate emissions from two flexible-fuel vehicles equipped with spark ignition engines, with one wall-guided direct injection and one port fuel injection configuration. Both vehicles were tested over triplicate Federal Test Procedure (FTP) and Unified Cycles (UC) using a chassis dynamometer. Emissions of nonmethane hydrocarbons (NMHC) and carbon monoxide (CO) showed some statistically significant reductions with higher alcohol fuels, while total hydrocarbons (THC) and nitrogen oxides ($NO_x$) did not show strong fuel effects. Acetaldehyde emissions exhibited sharp increases with higher ethanol blends for both vehicles, whereas butyraldehyde emissions showed higher emissions for the butanol blend relative to the ethanol blends at a statistically significant level. Particulate matter (PM) mass, number, and soot mass emissions showed strong reductions with increasing alcohol content in gasoline. Particulate emissions were found to be clearly influenced by certain fuel parameters including oxygen content, hydrogen content, and aromatics content.
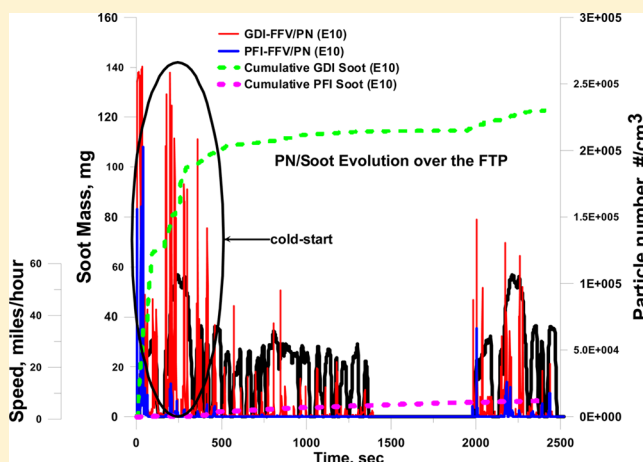
## INTRODUCTION

Ethanol is the world's most popular biofuel for use with existing spark-ignition (SI) engines.[1] In the U.S., the increase in ethanol use has been promoted by several legislative measures, including the Energy Independence and Security Act (EISA 2007) and the Renewable Fuel Standard (RFS), which was initiated in 2005 and expanded in 2007.[2] The latter mandates the use of 36 billion gallons of renewable fuels in the transportation fuel pool by 2022. Commercial U.S. gasoline contains ethanol 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 levels of alcohol fuels in gasoline, especially ethanol, are known as flexible fuel vehicles (FFVs) and are currently being offered by many manufacturers.

Currently, there is a widespread growth of gasoline direct injection (GDI) vehicles aiming at improving fuel economy over conventional port fuel injection (PFI) engines and reducing carbon dioxide ($CO_2$) emissions. Most GDI engines employ wall-guided designs, in which the fuel spray is directed from a side-mounted fuel injector toward a contoured piston and then upward toward the spark plug.[3] While wall-guided GDI engines offer advantages over their PFI counterparts, 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.[4,5]

Analogous to ethanol, higher alcohols have been the subject of increased interest as potential fuels in SI engines.[6,7] Particular emphasis has been given to butanol isomers, which combine the advantages of an energy density closer to that of gasoline with the oxygen content and renewability of ethanol.[8] Butanol isomers can be produced from biochemical pathways via fermentation using biomass-derived feedstocks, including corn, sugar cane, and cellulosic biomass.[8,9] Compared to ethanol, butanol isomers exhibit lower vapor pressure, are less corrosive, and less hydrophilic. However, the octane number and latent heat of vaporization of butanol isomers are lower than ethanol. Butanol

isomers contain less oxygen per unit volume compared to ethanol. This gives butanol isomers a higher lower heating value of 33.1 MJ/kg compared to 26.8 MJ/kg for ethanol, which more closely resembles the heating value of gasoline (42.7 MJ/kg).[10] These factors offer the potential for butanol isomers to be blended at higher blending levels in gasoline than ethanol under existing regulations and with current technology engine control systems, providing additional pathways to satisfy the volume targets set by the RFS.

The use of midlevel and higher level blends of ethanol has been widely investigated in older and modern technology FFVs,[11−14] while data on emissions from higher level butanol blends is more sparse.[15,16] Most chassis dynamometer studies on the effects of higher ethanol blends on tailpipe emissions have been conducted on FFVs equipped with PFI engines and generally focused on the regulated emissions and gaseous air toxic pollutants.[17,18] Haskew and Liberty[14] tested a fleet of seven 2006−2007 model year FFVs and did not find statistically significant fuel effects between E6 and E85 for most of the regulated emissions on most of the test cycles. Hubbard et al.[19] 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 nitrogen oxide ($NO_x$) and nonmethane hydrocarbon (NMHC) emissions compared to E0. Similar findings were seen by Yanowitz and co-workers[20] when they tested nine FFVs over the LA92 test procedure. They found reductions in $NO_x$, carbon monoxide (CO), and carbon dioxide ($CO_2$) as well as increases in emissions of ethanol, acetaldehyde, and formaldehyde with increasing ethanol concentration. Graham et al.[21] showed that the use of E85 resulted in statistically significant decreases in $NO_x$, NMHC, 1,3-butadiene, and benzene emissions relative to E0 over the FTP and statistically significant increases in formaldehyde and acetaldehyde. To date, there is limited data on PM emissions from FFVs equipped either with PFI or GDI engines. Recently, Mamakos and colleagues[22] found large reductions in particle number and PM mass emissions from a Euro 5 GDI-FFV with the use of 75−85% ethanol/gasoline blends over the New European Driving Cycle (NEDC) and the Artemis cycles. Reductions in particle number concentrations with E85 compared to gasoline were also seen in a study conducted by Lee et al.[23] when they tested a 2005 model year PFI-FFV over the NEDC. Magara-Gomez and co-workers[24] 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.

Because of the increasing penetration of GDI vehicles in the market together with the introduction of new alternative alcohol fuel formulations, there is a need to better characterize the emissions from modern technology on-road vehicles operating on new fuels to help quantify the contribution of these sources to ozone and ambient PM concentrations. This study reports the impacts of higher level ethanol and isobutanol blends on the gaseous and particulate emissions from two FFVs over the FTP and Unified Cycle (UC) that include both cold-starts and transient operation. This study represents one of the first studies to look at higher level ethanol blends and butanol blends in GDI vehicles. Results are discussed in the context of changing fuel type, fuel composition, and engine technology.

## EXPERIMENTAL SECTION

**Test Fuels and Vehicles.** A total of four 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 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 higher ethanol blends represent the upper and lower blend limits of the current E85 specification. Isobutanol was blended with gasoline at a proportion of 55% (Bu55) by volume. This was the highest volume of isobutanol that could be blended while still meeting the California summer gasoline specifications. The main physicochemical properties of the test fuels are provided in the Supporting Information, Table S1.

Testing was conducted on two late-model FFV pickup trucks with similar horsepower ratings and certification levels. This included a 2013 model year (MY) Ford F150 (PFI-FFV) with a 3.7 L V6 engine and PFI fueling having a rated horsepower of 302 hp at 6500 rpm and a 2014 MY Chevrolet Silverado (GDI-FFV) with a 5.3 L V8 engine and wall-guided direct injection fueling having a rated horsepower of 355 hp at 5600 rpm. Both vehicles were equipped with three-way catalysts (TWCs), were flexible-fuel capable, and were certified under California ULEV II/Tier 2 Bin 4 emission standards. The vehicles had accumulated mileages of 13700 for the Ford F150 and 2649 for the Chevrolet Silverado at the beginning of the test campaign.

**Driving Cycles and Measurement Protocol.** Each vehicle was tested on each fuel over three FTPs and three UC tests. 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. The preconditioning procedure was similar to that specified in the Code of Federal Regulations (40 CFR 86.132-00). For each fuel change there were multiple drain and fills and 2 LA4s along with idle periods 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 can be found elsewhere.[25]

**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-in. single-roll electric dynamometer. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system was used to obtain certification-quality emissions measurements. For all tests, standard bag measurements were obtained for THC, CO, $NO_x$, NMHC, and $CO_2$. NMHC was determined from the combined results from the THC analyzer and a separate methane ($CH_4$) analyzer. NMHC was not corrected for oxygenated species as ethanol exhaust emissions were not measured. Bag measurements were made with a Pierburg AMA-4000 bench. Detailed information regarding the collection and analysis methodology for carbonyl compounds and 1,3-butadiene, benzene, toluene, ethylbenzene, and xylene compounds, as well as for PM mass, particle number, particle size distributions, and soot mass emissions are provided in the Supporting Information.

## RESULTS AND DISCUSSION

**THC and NMHC Emissions.** THC emissions for both FFVs over the FTP and UC are shown in Figure 1a, while a detailed representation of the phase-specific and weighted THC emissions is provided in Tables S2 and S3 in the Supporting Information. The differences between results for different test fuels were evaluated statistically to determine if there were any statistically significant differences between fuels. Systat 13 was
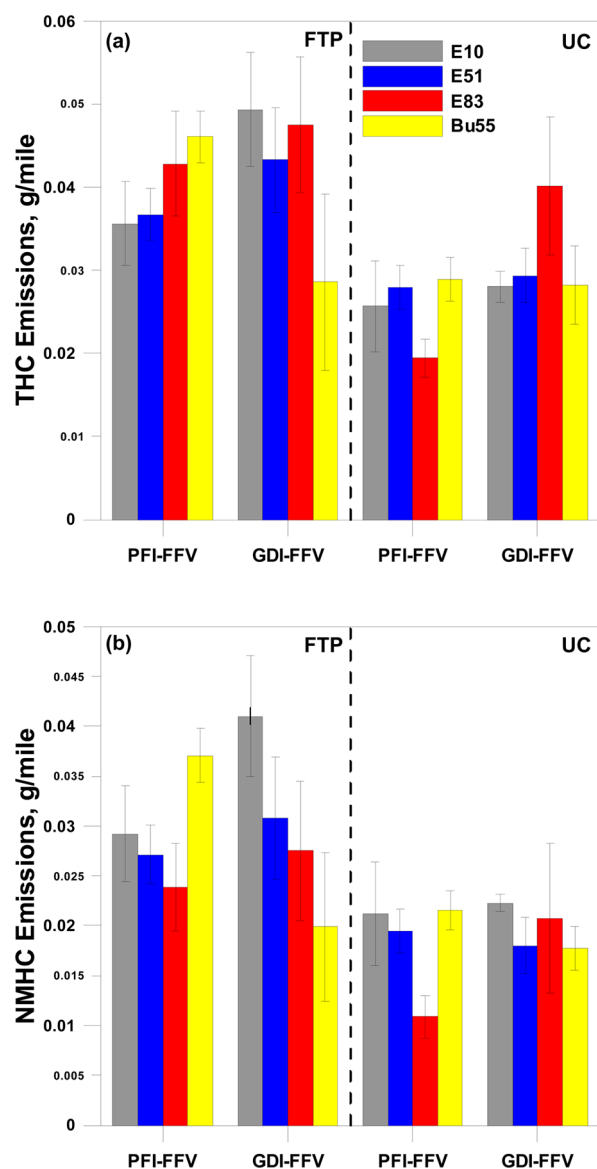
**Figure 1.** THC (a) and NMHC (b) emissions for the PFI-FFV and GDI-FFV. Error bars represent ± one standard deviation around the average value for each fuel.

used for the statistical analysis for this and subsequent sections, as detailed further in the Supporting Information. There were no statistically significant differences between any fuels in weighted THC or NMHC emissions for either test cycle. For the hot-start phase of the FTP, THC emissions showed statistically significant reductions of 38% for Bu55 compared to E10 and 46% for E83 compared to Bu55. Similar to THC, weighted NMHC emissions did not show any strong fuel trends over either test cycle, with the exception of E83 showing a 32% decrease in NMHC emissions compared to E10 for the UC at a marginally statistically significant level (Figure 1b). For the hot-start phase of the FTP, E51 and E83 blends showed statistically significant decreases in NMHC emissions of 80% and 5%, respectively, relative to E10. A 72% decrease for Bu55 relative to E10 at a marginally statistically significant level was also found for the hot-start phase of the FTP.

Published studies of the impact of higher ethanol blends on THC/NMHC emissions from FFVs generally show reductions with increasing alcohol content in the fuel, which could be ascribed to the fuel-bound oxygen.[17,19] The results reported here

did not show a global trend for THC/NMHC emissions and agree with those presented by Karavalakis et al.,[13] although that study did show increases in THC/NMHC emissions for E85 with a PFI-FFV. Statistically insignificant fuel effects for NMHC for the FTP and UC were also seen in previous studies.[14] The influence of the cold-start was especially strong in THC/NMHC emissions with the majority of these emissions being released during the first 200−300 s of the cycle. The higher cold-start THC/NMHC emissions are due to the TWC being below its light-off operating temperature. THC emissions for the hot-running and hot-start phases were practically eliminated due to the efficient oxidation of hydrocarbon fuel fractions by the TWC. For the GDI-FFV, THC emissions were generally higher compared to the PFI-FFV, which could be from incomplete evaporation of fuel trapped in the piston top land crevice due to fuel impingement effects.[4] This phenomenon would be particularly pronounced during the cold-start phase. The lower THC/NMHC emissions during the hot-running and hot-start phases could also be due to the increased cylinder surface temperatures that aid better fuel vaporization and minimizes pool fires.

**CO and $NO_x$ Emissions.** Figure 2a shows that the use of higher ethanol blends and the isobutanol blend led to some large reductions in CO emissions over both cycles. For the FTP, weighted CO emissions showed statistically significant decreases of 37% and 30%, respectively, for E83 relative to E10 and Bu55. For the cold-start and hot-start phases of the FTP, E83 showed a marginally statistically significant decrease of 36% and a statistically significant decrease of 58%, respectively, compared to E10. For the UC, E83 showed weighted CO emissions that were lower at a statistically significant level compared to E10 (48%), E51 (50%), and Bu55 (46%). Analogous to the weighted emissions, E83 showed statistically significant lower CO emissions for the cold-start and hot-running phases of the UC compared to E10, E51, and Bu55. Reductions in CO emissions with higher ethanol blends have also been seen in previous studies and was ascribed to the increase in the oxygen content in the fuel.[26,27] The reductions in CO emissions reported here for E51 and E83 could also be a consequence of the lower 50% distillation temperature (T50) for these fuels compared to E10. This is in agreement with a previous study conducted by Durbin and co-workers[28] where they found reduced CO emissions with lower T50 in ethanol blends. This is also in agreement with the findings of the EPAct study of fuel property effects on emissions, 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.[29] This phenomenon was not consistent for the isobutanol blend, which had a higher T50 than E10 and showed comparable or higher CO emissions for the PFI-FFV but lower for the GDI-FFV compared to E10.

Figure 2b presents $NO_x$ emissions as a function of fuel type. $NO_x$ emissions showed discordant results for the test fuels for both vehicles. While some fuel trends were seen over the cold-start phase of the FTP, statistical analyses for the two vehicles showed that $NO_x$ emissions did not show any statistically significant differences for the weighted, hot-running, and hot-start phases of the UC. The only statistically significant effect on $NO_x$ emissions was observed during the cold-start phase of the FTP for E83 that showed a reduction of 50% compared to E10. Previous studies have shown that $NO_x$ emissions can increase with higher ethanol blends, although this trend is not consistent between studies and is stronger in older vehicles,[13] while other
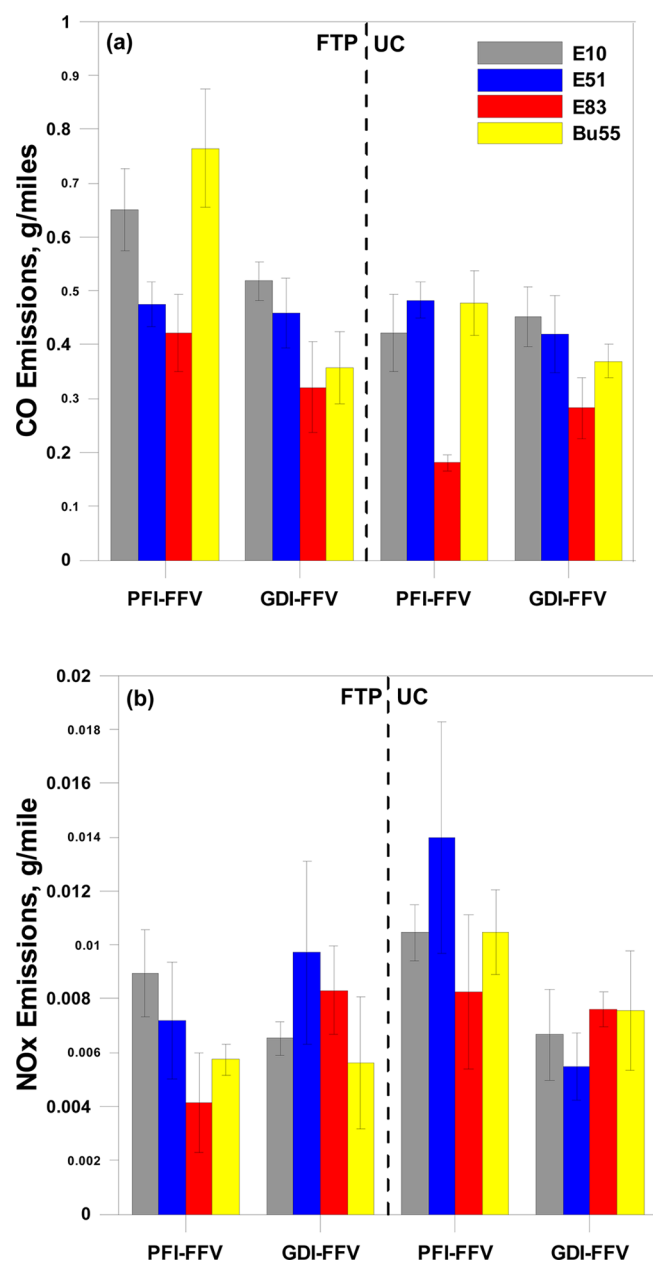
**Figure 2.** CO (a) and $NO_x$ (b) emissions for the PFI-FFV and GDI-FFV. Error bars represent $\pm$ one standard deviation around the average value for each fuel.

studies have shown some reductions in $NO_x$ or no change with higher ethanol blends.[14,26] The lack of fuel impacts in $NO_x$ emissions reported here could be due to a certain extent to improvements in aftertreatment technologies and advanced engine calibration.

**Greenhouse Gas (GHG) Emissions and Fuel Economy.** The use of higher ethanol blends and the isobutanol blend resulted in increases in $CH_4$ emissions for both vehicles over the FTP and UC, as shown in the Supporting Information (Figure S1). For the FTP, the blends of E51 and E83 showed statistically significant increases in weighted $CH_4$ emissions of 54% and 63%, respectively, compared to E10. For the UC, weighted $CH_4$ emissions showed statistically significant increases of 49%, 61%, and 41%, respectively, for E51, E83, and Bu55 compared to E10. Emissions of $CO_2$ are presented in the Supporting Information (Figure S2). For the FTP, $CO_2$ emissions did not

show any strong fuel effects for either of the test vehicles. For the UC, weighted $CO_2$ emissions showed marginally statistically significant reductions of 4% for E83 compared to both Bu55 and E10 and a statistically significant reduction of 6% for E83 compared to E51.

Fuel economy for each vehicle/fuel combination is presented in the Supporting Information (Figure S3). Fuel economy was calculated on the basis of the carbon balance method and the unique properties for each different test fuel. Overall, our results showed that fuel economy was lowered with increasing alcohol concentration/reducing energy content in the fuel. For the FTP, weighted fuel economy showed statistically significant reductions of 13%, 33%, and 7%, respectively for E51, E83, and Bu55 compared to E10. The same phenomenon was also seen for the UC, with fuel economy showing statistically significant reductions of 17%, 30%, and 8%, respectively, for E51, E83, and Bu55 compared to E10. For comparison, the energy content of the E51, E83, and Bu55 fuels were lower by 17%, 36%, and 10%, respectively, compared to E10, similar to the reductions seen in the fuel economy.

**Carbonyl Emissions.** Carbonyl emissions are shown in Figure 3. Carbonyl emissions were only measured over the FTP. Formaldehyde and acetaldehyde were the most abundant aldehydes in the tailpipe, followed by butyraldehyde, benzaldehyde, propionaldehyde, hexanaldehyde, methacrolein, and crotonaldehyde. Some trends toward higher formaldehyde emissions with E83 and Bu55 relative to E10 for the PFI-FFV were seen, but not for the GDI-FFV. Overall, there were not any fuel effects for weighted formaldehyde emissions; however, for the cold-start phase E83 and Bu55 showed statistically significant increases of 88% and 110%, respectively, compared to E10. Other studies have also reported higher formaldehyde emissions with ethanol and isobutanol blends.[13,17,30,31] For ethanol, H abstraction from the OH moiety yields an ethoxy radical ($CH_3CH_2O^\bullet$), which $\beta$-scissions to form $CH_3$ and formaldehyde.[32] For isobutanol, formaldehyde is produced through the oxidation of methyl radicals to form $CH_3O$ and hydroxyl radicals that in turn yield formaldehyde. Formaldehyde is also formed by $\beta$-scission decomposition of the $C_4H_8OH$ radical.[33,34]

Acetaldehyde emissions showed dramatic increases with the higher ethanol blends. For the weighted acetaldehyde emissions, E51 and E83 showed statistically significant increases of 380% and 580% compared to E10 and 375% and 572% compared to Bu55. A similar picture was also seen for the cold-start phase, with both E51 and E83 fuels showing statistically significant increases in acetaldehyde emissions compared to E10 and Bu55. Acetaldehyde is principally formed due to the partial oxidation of ethanol, which explains the tendency for acetaldehyde to increase with ethanol concentration.[35] Abstraction of a secondary H atom leads to the $\alpha$-hydroxyethyl radical ($CH_3CHOH$), which either reacts with $O_2$ or unimolecularly decomposes to yield a radical and acetaldehyde.[32]

For the isobutanol blend, a trade-off was seen between butyraldehyde and acetaldehyde emissions, with butyraldehyde emissions showing increases and acetaldehyde showing decreases relative to higher ethanol blends. For the weighted butyraldehyde emissions, the Bu55 fuel showed statistically significant increases of 261%, 646%, and 269%, respectively, compared to E10, E51, and E83. The higher butyraldehyde emission results with Bu55 are consistent with the studies of Ratcliff et al.[30] and Karavalakis et al.[16] It was hypothesized that butyraldehyde was produced via sequential H atoms abstractions from the isobutanol hydroxyl moiety to form a $C_4H_9O$ radical,
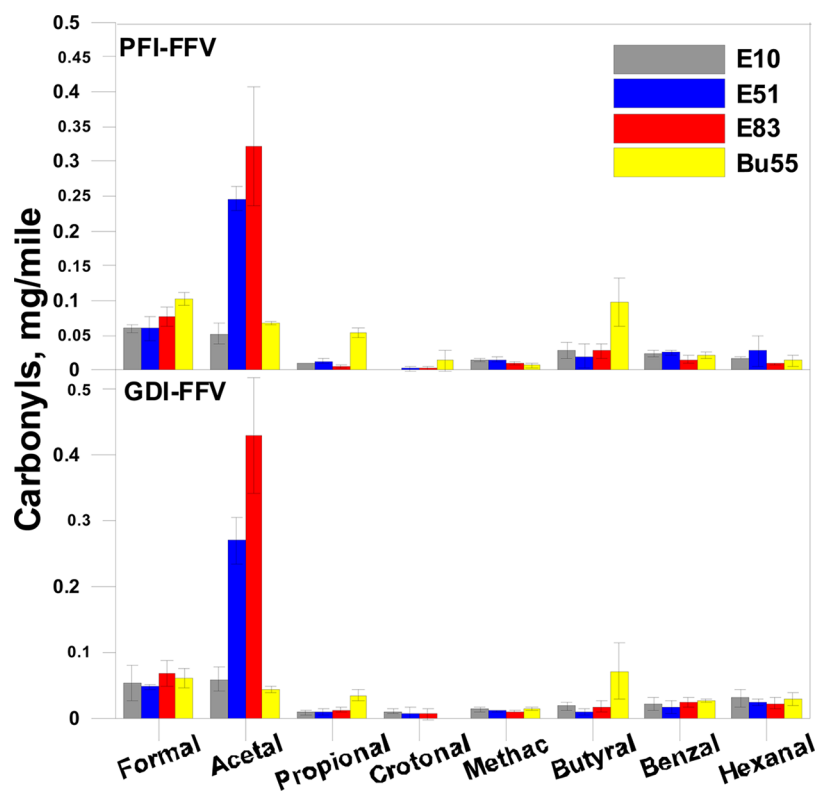
**Figure 3.** Carbonyl emissions for the PFI-FFV and GDI-FFV over the FTP cycle as a function of fuel type. Error bars represent ± one standard deviation around the average value for each fuel.



**Figure 4.** Emissions of 1,3-butadiene and BTEX for the PFI-FFV and GDI-FFV over the FTP cycle as a function of fuel type. Error bars represent ± one standard deviation around the average value for each fuel.

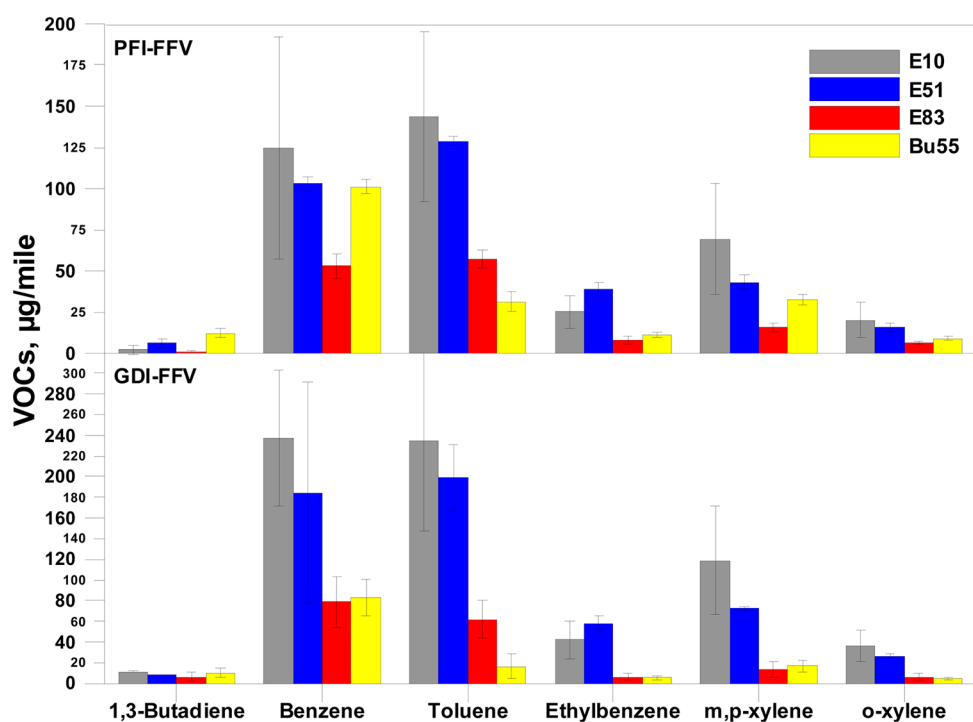which then undergoes $\beta$-scission to yield butyraldehyde.[36] For the weighted propionaldehyde emissions, E10, E51, and E83 showed statistically significant decreases of 81%, 78%, and 82%, respectively, compared to Bu55. For the isobutanol blend, the formation pathway for propionaldehyde was stronger than that

of ethanol. Sarathy et al.[33] attribute propionaldehyde formation from butanol through 1-propenol via H- and/or $HO_2$-assisted enol−keto isomerization. Although some decreasing trends with the higher alcohol fuels were seen for benzaldehyde, hexanaldehyde, and methacrolein emissions, these differences

were not statistically significant when statistical analyses over the two vehicles was applied.

**Selected Volatile Hydrocarbons.** Figure 4 presents the FTP-based 1,3-butadiene, benzene, ethylbenzene, toluene, *m/p*-xylene, and *o*-xylene emissions. The monoaromatic hydrocarbons of benzene, ethylbenzene, toluene, *m/p*-xylene, and *o*-xylene are commonly referred to as BTEX. For both vehicles, the principally detected compounds in the emissions were toluene and benzene followed by *m/p*-xylene and ethylbenzene. The GDI-FFV BTEX emissions were about twice those for the PFI-FFV, which is an interesting finding since the NMHC values are similar for the two vehicles. Benzene emissions for E83 showed statistically significant decreases of 60% and 58%, respectively, relative to E10 and E51. For toluene, ethylbenzene, *m/p*-xylene, and *o*-xylene compounds as a group, the statistically significant reductions in emissions ranged from 66% to 85% for E83 compared to E10, from 66% to 84% for E83 compared to E51, from 76% to 88% for Bu55 compared to E10, and from 54% to 89% for Bu55 compared to E51. Emissions of 1,3-butadiene were found at very low concentrations for both vehicles and did not show any strong fuel effects. Although some increases in 1,3-butadiene emissions were seen for Bu55 relative to the ethanol blends for the PFI-FFV, these differences were not statistically significant looking at the two vehicles combined.

**Particulate Matter, Soot Mass, and Particle Number Emissions.** Cycle-based PM mass emissions are shown in Figure 5a. The PM mass emissions of the GDI-FFV were somewhat higher than those of the PFI-FFV, particularly for the E10 base fuel. Our results are in agreement with previous studies showing higher PM mass emissions with GDI vehicles compared to their PFI counterparts.[37,38] Higher PM emissions from GDI engines can be ascribed to fuel impingement on the piston and cylinder surfaces (pool fires), which may result in liquid fuel that is not totally vaporized and well mixed with intake air at the start of the combustion, leading to charge heterogeneity and localized fuel-rich regions in the charge cloud. Unlike GDI operation, in PFI engines the fuel is injected and vaporized on the intake ports, achieving a high degree of mixture homogeneity at the spark event.[39−41] Although for the FTP for the PFI-FFV some increases in PM emissions were seen with the higher ethanol blends and the isobutanol blend relative to E10, statistical analysis showed that there were no strong fuel effects on PM emissions during FTP operation for the two vehicles combined. For the UC, on the other hand, PM emissions showed statistically significant decreases for E51 and E83 of 61% and 59%, respectively, compared to E10 and a marginally statistically significant decrease of 52% for Bu55 compared to E10. The reductions in PM emissions reported here could be a consequence of the increased oxygen content and/or the lower hydrocarbon content for the higher ethanol blends and isobutanol blend.[42,43]

Soot mass emissions are shown in the Supporting Information (Figure S4). Note that the Micro Soot Sensor (MSS) was not available for the E83 testing for the GDI-FFV for the UC. The trend for soot mass emissions agreed qualitatively well with the filter-based PM mass and number emissions for the GDI-FFV but not for the PFI-FFV. It is noteworthy that soot emissions remained nearly constant for the PFI-FFV regardless of alcohol content, which is in contrast with the trend of PM mass emissions rate over the FTP test. The GDI-FFV exhibited substantially higher soot emissions than the PFI-FFV, suggesting that the PM from the GDI-FFV was primarily elemental carbon in nature.[43] The use of higher ethanol blends and the isobutanol blend
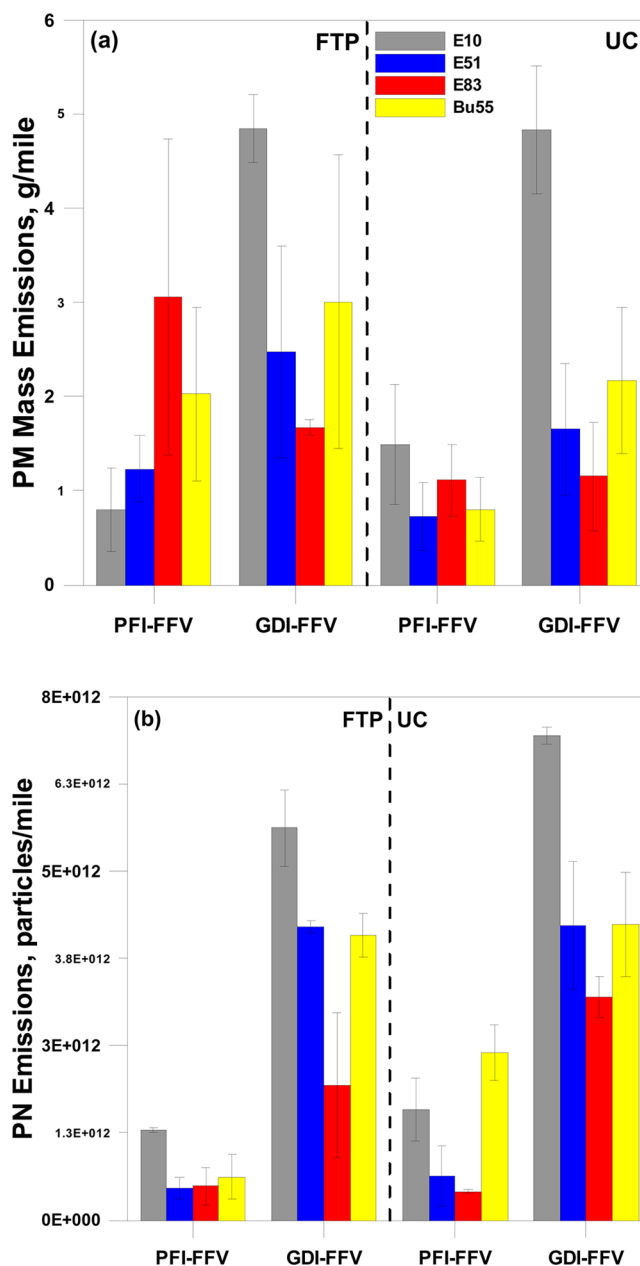


**Figure 5.** PM mass (a) and PN (b) emissions for the PFI-FFV and GDI-FFV. Error bars represent ± one standard deviation around the average value for each fuel.

resulted in sharp, statistically significant reductions in soot emissions relative to E10 for both vehicles. Overall, the lower soot emissions for the higher alcohol fuels could be due to the increased oxygen content in the blends, which facilitates more complete combustion,[44] or the lower hydrocarbon content. Such phenomena were not seen for the PFI-FFV due to the nature of well premixed combustion. Soot emissions were slightly higher for the UC compared to FTP, which can be ascribed to the more transient driving nature of UC. As shown in Figure 5a, PM mass emission rates showed different trends compared to those of soot mass emissions. For the FTP, for the PFI-FFV, it is possible that organic carbon or semivolatile PM mass increases as alcohol content increases. This is also confirmed with the average particle size distributions, as shown in the following sections, where no such trend as the PM mass emissions rates by gravimetric method was observed. In addition, strong correlations were seen

between soot formation and aromatic content, as well as the fuel hydrogen content. For fuels with lower aromatic contents, and corresponding higher H/C ratios, there was lower soot in the exhaust. Under the present test conditions, the dependence of soot formation on fuel aromatic content could be stronger than that based on the H/C ratio, as will be discussed in the following paragraphs.

Figure 5b shows the particle number (PN) emissions, with the GDI-FFV showing higher particle counts than the PFI-FFV. Note that PN emissions do not necessarily agree with PM mass for the PFI-FFV, but they tend to corroborate well for the GDI-FFV. Higher PN emissions for GDI vehicles in relation to PFI vehicles have been reported in previous studies.[16,38] For the FTP, weighted PN emissions for E83 and Bu55 showed a statistically significant decrease of 59% and a marginally statistically significant decrease of 52%, respectively, compared to E10. For the cold-start phase of the FTP, a marginally statistically significant decrease was seen for E83 compared to E10, while for the hot-running and hot-start phases statistically significant reductions were observed for E51, E83, and Bu55 compared to E10. For the UC, weighted PN emissions for E51 and E83 showed statistically significant decreases of 50% and 64%, respectively, relative to E10, whereas E83 showed a statistically significant reduction of 65% and E51 a marginally statistically significant reduction of 52% compared to Bu55. For the cold-start phase of the UC, E51 and E83 showed a statistically significant and a marginally statistically significant reduction, respectively, compared to E10. For the hot-running phase, E83 was lower at a statistically significantly level compared to E10 and Bu55, while for the hot-start phase E51 showed lower PN relative to E10, at a marginally statistically significant level.

The fuel effect on PN emissions was particularly noticeable, with higher oxygen content in the fuel probably being the main contributing factor for the PN decrease by suppressing soot formation. Another important parameter worth considering is the aromatics content. Our results showed that PN/PM mass emissions correlated reasonably well with the content of aromatic compounds in the fuels, especially the multisubstituted aromatics. It should be noted that the isobutanol blend had lower total aromatics content than E51 and E83, but showed higher PN emissions compared to these fuels. A combination of factors could contribute to the increase in PN emissions for the Bu55 blend, including the lower oxygen content compared to E51 and E83, and the higher content of heavier monoaromatic and naphtheno-aromatic hydrocarbons with high boiling points relative to E83.[45] An additional contributing factor for the higher PN emissions could be that branched butanols can produce intermediate higher molecular weight radicals than ethanol, which react to produce higher molecular weight soot products.[46] In addition, the cold-start influence was also noticeable in PN emissions (Tables S2 and S3, Supporting Information), with the majority of particles emitted during the beginning of the FTP and UC when the engine and TWC are not yet at operating temperature. This phenomenon was particularly evident for the PFI-FFV where the cold-start phase dominated PN emissions, but not for the GDI-FFV where particles were produced over the entire duration of the cycle. Cold-start PN emissions for the UC were markedly higher than 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 more operation after the TWC has reached its light-off temperature and the engine is warmed up.

**Particle Size Distributions (PSDs).** Parts a and b of Figure 6 display the PSDs for the PFI-FFV and GDI-FFV, respectively.
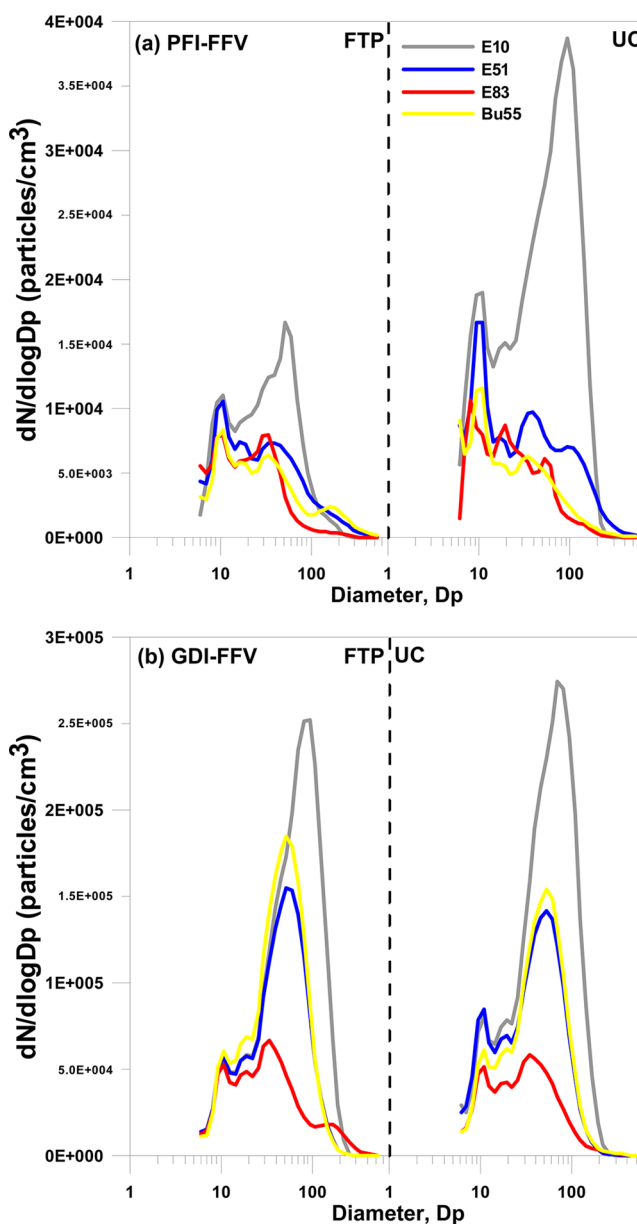


**Figure 6.** Average particle size distributions for the PFI-FFV (a) and GDI-FFV (b). Error bars represent ± one standard deviation around the average value for each fuel.

For the PFI-FFV, the PSD profiles for both test cycles did not show clear peaks, especially for E83 and Bu55 blends. Most fuels showed emissions of nucleation mode particles in the size range of 10−30 nm, with the exception of E10 that showed a decidedly bimodal PSD with nucleation mode particles peaking at 11 nm for both cycles and accumulation mode particles in the size range of 53 and 93 nm, respectively, for FTP and UC. Based on the very low soot mass emissions for the PFI-FFV, it is theorized that the bulk of these particles consist mostly of semivolatile organic and sulfur compounds. The GDI-FFV displayed a diesel-like bimodal distribution with the accumulation mode dominating the PSD. The accumulation mode geometric mean particle diameter ranged from 34 nm (E83) to 93 nm (E10) for the FTP and from

34 nm (E83) to 70 nm (E10) for the UC. The peak particle size of the nucleation mode centered near 11 nm for both cycles.

The fuel impact on PSDs was particularly clear with the high oxygen content low aromatics content blends showing lower number concentrations of accumulation mode particles. The higher oxygen/lower aromatic content E51 and E83 systematically showed lower number concentrations of accumulation mode particles, and in most cases a smaller size in geometric mean diameter compared to the other blends. This is in good agreement with the sharp reductions in soot mass emissions with the higher ethanol blends, as shown in the Supporting Information (Figure S4). It is assumed that the oxygen content and the lower aromatics content in the blends contributed to lower soot formation rates, thus reducing the number of accumulation mode particles. In addition, the lower combustion temperatures with increasing alcohol content in gasoline could have some influence on the reduction in accumulation mode particles with higher ethanol blends. Under these conditions, primary carbon particles formed by thermal pyrolysis and dehydrogenation reactions of fuel usually decrease.[7]

**Implications.** This study revealed that the employment of higher alcohol fuels for a PFI-FFV and GDI-FFV could lead to emission changes of GHGs, CO, aldehydes, BTEX, and particulates. This study showed that higher alcohol fuels would decrease PM mass and number emissions, while current technology direct injection fueling produces higher particle number and soot mass emissions than the PFI fueling as a result of liquid fuel wetting effects and insufficient air fuel mixing. Our results also suggest that BTEX emissions would decrease with the deployment of higher ethanol blends and the isobutanol blend, which is an important finding since benzene is a known carcinogen to humans and these other compounds play an active role in the atmospheric chemistry and contribute to the photochemical smog present in many metropolitan areas. On the other hand, the use of higher ethanol blends in FFVs would dramatically increase acetaldehyde emissions, which has been classified by the National Institute of Occupational Safety and Health (NIOSH) and by the International Agency for Research on Cancer (IARC) as a potential human carcinogen. Emphasis should be given to the higher butyraldehyde emissions with the use of isobutanol blend, given the fact that butyraldehyde possesses similar reactivity and mutagenicity to acetaldehyde. As such, the results reported here may have important implications, given the attention butanol is gaining as an automotive fuel. Overall, this study suggests that more work on the chemical, toxicological, and biological characterization of PM emissions from GDI vehicles using higher ethanol and butanol blends would help to provide a better understanding on their potential environmental and health implications. In terms of GHGs, the impact of the higher alcohol fuels was mixed, with the higher alcohol fuels showing some increases in $CH_4$ emissions, but the E83 fuel also showing some reductions in $CO_2$ emissions over the UC cycle. Overall, the differences in tailpipe GHGs between fuels are probably relatively minor compared to other factors that might influence a full life cycle analysis assessment of GHGs for different fuels. The PM emission levels for these vehicles on the low level ethanol blend (i.e., E10) are 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 are clearly above the ultralow 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 this current technology GDI-FFV. For GDI-FFVs, this would likely be achieved by a combination of engine calibration and different fuel injection design, such as a spray-guided architecture. Higher levels of fuel oxygenates could also potentially provide PM reduction benefits for future GDI and PFI vehicles.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Further details on the statistical analysis, fuel properties, and the emissions of $CH_4$, $CO_2$, soot mass, as well as fuel economy are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) Yan, X.; Inderwildi, O. R.; King, D. A.; Boies, A. M. Effects of ethanol on vehicle energy efficiency and implications on ethanol life-cycle greenhouse gas analysis. *Environ. Sci. Technol.* **2013**, *47*, 5535−5544.

(2) U.S. Environmental Protection Agency. *Fuels and Fuel Additives, Renewable Fuel Standard*; http://www.epa.gov/otaq/fuels/renewablefuels (accessed Oct 2, 2014).

(3) Alkidas, A. C. Combustion advancements in gasoline engines. *Energy Convers. Manage.* **2007**, *48*, 2751−2761.

(4) Zhao, F.; Lai, M. C.; Harrington, D. Automotive spark-ignited direct-injection gasoline engines. *Prog. Energy Combust. Sci.* **1999**, *25*, 437−562.

(5) Stevens, E.; Steeper, R. Piston wetting in an optical DISI Engine: fuel films, poolfires, and soot generation. *SAE Int. J. Engines* **2001**, *110*, 1287−1294.

(6) Irimescu, A. Performance and fuel conversion efficiency of a spark ignition engine fueled with isobutanol. *Appl.Energy* **2012**, *96*, 477−483.

(7) Zhang, Z.; Wang, T.; Jia, M.; Wei, Q.; Meng, X.; Shu, G. Combustion and particle number emissions of a direct injection spark ignition engine operating on ethanol/gasoline and n-butanol/gasoline blends with exhaust gas recirculation. *Fuel* **2014**, *130*, 177−188.

(8) Xue, C.; Zhao, X. Q.; Liu, C. G.; Chen, L. J.; Bai, F. W. Prospective and development of butanol as an advanced biofuel. *Biotechnol. Adv.* **2013**, *31*, 1575−1584.

(9) Tao, L.; Tan, E. C. D.; McCormick, R. L.; Zhang, M.; Aden, A.; He, X.; Zigler, B. T. Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol. *Biofuels, Bioprod. Biorefin.* **2014**, *8*, 30−48.

(10) Wallner, T.; Miers, S. A.; McConnell, S. A comparison of ethanol and butanol as oxygenates using a direct-injection, spark-ignition engine. *J. Eng. Gas Turbines Power* **2009**, *131*, 1−9.

(11) West, B. H.; Lopez, A. J.; Theiss, T. J.; Graves, R. L.; Storey, J. M.; Lewis, S. A. Fuel economy and emissions of the ethanol-optimized Saab 9-5 Biopower. *SAE [Tech. Pap.]* **2007**, 200701-3994.

14023

dx.doi.org/10.1021/es5034316 | *Environ. Sci. Technol.* 2014, 48, 14016−14024

(12) Yassine, H. M.; La Pan, M. Impact of ethanol fuels on regulated tailpipe emissions. *SAE [Tech. Pap.]* **2012**, 201201-0872.

(13) Karavalakis, G.; Durbin, T. D.; Shrivastava, M.; Zheng, Z.; Villela, M.; Jung, H. Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles. *Fuel* **2012**, *93*, 549−558.

(14) Haskew, H. M.; Liberty, T. F. Exhaust and evaporative emissions testing of flexible-fuel vehicles. Final Report to the Coordinating Research Council (CRC) under project E-80, 2011; http://www.crcao.org/reports/recentstudies2011/E-80/E-80%20Final%20Report+Appendices.pdf.

(15) Dernotte, J.; Mounaim-Rousselle, C.; Halter, F.; Seers, P. Evaluation of butanol-gasoline blends in a port fuel-injection, spark-ignition engine. *Oil Gas Sci. Technol.-Rev. IFP* **2010**, *65*, 345−351 (accessed September 1, 2012).

(16) Karavalakis, G.; Short, D.; Vu, D.; Villela, M.; Asa-Awuku, A.; Durbin, T. Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and isobutanol blends. *Fuel* **2014**, *128*, 410−421.

(17) Schulz, M.; Clark, S. Vehicle emissions and fuel economy effects of 16% butanol and various ethanol blended fuels (E10, E20, and E85). *J. ASTM Int.* **2011**, *8*, 1−19.

(18) Yanowitz, J.; McCormick, R. L. Effect of E85 on tailpipe emissions from light-duty vehicles. *J. Air Waste Manage. Assoc.* **2009**, *59*, 172−182.

(19) Hubbard, C. P.; Anderson, J. E.; Wallington, T. J. Ethanol and air quality: Influence of fuel ethanol content on emissions and fuel economy of flexible fuel vehicles. *Environ. Sci. Technol.* **2014**, *48*, 861−867.

(20) Yanowitz, J.; Knoll, K.; Kemper, J.; Luecke, J.; McCormick, R. L. Impact of Adaptation on flex-fuel vehicle emissions when fueled with E40. *Environ. Sci. Technol.* **2013**, *47*, 2990−2997.

(21) Graham, L. A.; Belisle, S. L.; Baas, C. L. Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85. *Atmos. Environ.* **2008**, *42*, 4498−4516.

(22) Mamakos, A.; Martini, G.; Marotta, A.; Manfretti, U. Assessment of different technical options in reducing particle emissions from gasoline direct injection vehicles. *J. Aerosol Sci.* **2013**, *63*, 115−125.

(23) Lee, H.; Myung, C. L.; Park, S. Time-resolved particle emission and size distribution characteristics during dynamic engine operation conditions with ethanol-blended fuels. *Fuel* **2009**, *88*, 1680−1686.

(24) Magara-Gomez, K. T.; Olson, M. R.; McGinnis, J. E.; Zhang, M.; Schauer, J. J. Effect of ambient temperature and fuel on particle number emissions on light-duty spark-ignition vehicles. *Aerosol Air Quality Res.* **2014**, *14*, 1360−1371.

(25) Karavalakis, G.; Short, D.; Hajbabaei, M.; Vu, D.; Villela, M.; Russell, R.; Durbin, T.; Asa-Awuku, A. Criteria Emissions, Particle Number Emissions, Size Distributions, and Black Carbon Measurements from PFI Gasoline Vehicles Fuelled with Different Ethanol and Butanol Blends. *SAE [Tech. Pap.]* **2013**, 201301−1147.

(26) Dardiotis, C.; Fontaras, G.; Marotta, A.; Martini, G.; Manfredi, U. Emissions of modern light duty ethanol flex-fuel vehicles over different operating and environmental conditions. *Fuel* **2015**, *140*, 531−540.

(27) Costagliola, M. A.; De Simio, L.; Iannaccone, S.; Prati, M. V. Combustion efficiency and engine out emissions of a S.I. engine fueled with alcohol/gasoline blends. *Appl. Energy* **2013**, *111*, 1162−1171.

(28) Durbin, T. D.; Miller, J. W.; Younglove, T.; Huai, T.; Cocker, K. Effects of fuel ethanol content and volatility on regulated and unregulated exhaust emissions for the latest technology gasoline eehicles. *Environ. Sci. Technol.* **2007**, *41*, 4059−4064.

(29) U.S. Environmental Protection Agency. Assessing the effect of five gasoline properties on exhaust emissions from light-duty vehicles certified to Tier 2 standards: Analysis of data from EPAct phase 3 (EPAct/V2/E-89). Final Report. EPA-420-R-13-002, April, 2013, http://www.epa.gov/otaq/models/moves/epact.htm (accessed May 30, 2013).

(30) Ratcliff, M. A.; Luecke, J.; Williams, A.; Christensen, E. D.; Yanowitz, J.; Reek, A.; McCormick, R. L. Impact of higher alcohols blended in gasoline on light-duty vehicle exhaust emissions. *Environ. Sci. Technol.* **2013**, *47*, 13865−13872.

(31) Wallner, T.; Frazee, R. Study of regulated and non-regulated emissions from combustion of gasoline, alcohol fuels and their blends in a DI-SI engine. *SAE [Tech. Pap.]* **2010**, *2010*, 011571.

(32) Haas, F. M.; Chaos, M.; Dryer, F. L. Low and intermediate temperature oxidation of ethanol and ethanol-PRF blends: An experimental and modeling study. *Combust. Flame* **2009**, *156*, 2346−2350.

(33) Sarathy, S. M.; Vranckx, S.; Yasunaga, K.; Mehl, M.; Oswald, P.; Metcalfe, W. K.; Westbrook, C. K.; Pitz, W. J.; Kohse-Hoinghaus, K.; Fernandes, R. X.; Curran, H. J. A comprehensive chemical kinetic combustion model for the four butanol isomers. *Combust. Flame* **2012**, *159*, 2028−2055.

(34) Broustail, G.; Halter, F.; Seers, P.; Moreac, G.; Mounaim-Rousselle, C. Comparison of regulated and non-regulated pollutants with iso-octane/butanol and iso-octane/ethanol blends in a port-fuel injection spark-ignition engine. *Fuel* **2012**, *94*, 251−261.

(35) Zervas, E.; Montagne, X.; Lahaye, J. Emission of alcohols and carbonyl compounds from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio. *Environ. Sci. Technol.* **2002**, *36*, 2414−2421.

(36) Moss, J. T.; Berkowitz, A. M.; Oehlschlaeger, M. A.; Biet, J.; Warth, V.; Glaude, P. A.; Battin-Leclerc, F. An experimental and kinetic modeling study of the oxidation of the four isomers of butanol. *J. Phys. Chem. A* **2008**, *112*, 10843−10855.

(37) Li, Y.; Xue, J.; Johnson, K.; Durbin, T.; Villela, M.; Pham, L.; Hosseini, S.; Short, D.; Karavalakis, G.; Asa-Awuku, A.; Jung, H. Determination of Suspended Exhaust PM Mass for Light Duty Vehicles Using IPSD Method. *SAE [Tech. Pap.]* **2014**, *2014*, 01-1594.

(38) Zhang, S.; McMahon, W. Particulate emissions for LEV II light-duty gasoline direct injection vehicles. *SAE Int. J. Fuels Lubr.* **2012**, *5*, 637−646.

(39) Maricq, M. M.; Szente, J. J.; Adams, J.; Tennison, P.; Rumpsa, T. Influence of mileage accumulation on the particle mass and number emissions of two gasoline direct injection vehicles. *Environ. Sci. Technol.* **2013**, *47*, 11890−11896.

(40) Piock, W.; Hoffmann, G.; Berndorfer, A.; Salemi, P.; Fusshoeller, B. Strategies towards meeting future particulate matter emission requirements in homogeneous gasoline direct injection engines. *SAE Int. J. Engines* **2011**, *4*, 1455−1468.

(41) Szybist, J. P.; Youngquist, A. D.; Barone, T. L.; Storey, J. M.; Moore, W. R.; Foster, M.; Confer, K. Ethanol blends and engine operating strategy effects on light-duty spark ignition engine particle emissions. *Energy Fuels* **2011**, *25*, 4977−4985.

(42) Storey, J. M.; Barone, T.; Norman, K.; Lewis, S. Ethanol blend effects on direct injection spark-ignition gasoline vehicle particulate matter emissions. *SAE Int. J. Fuels Lubr.* **2010**, *3*, 650−659.

(43) Maricq, M. M.; Szente, J. J.; Jahr, K. The impact of ethanol fuel blends on PM emissions from a light-duty GDI vehicle. *Aerosol Sci. Technol.* **2012**, *46*, 576−583.

(44) Wang, C.; Xu, H.; Herreros, J. M.; Lattimore, T.; Shuai, S. Fuel effect of particulate matter composition and soot oxidation in a direct-injection spark ignition (DISI) engine. *Energy Fuels* **2014**, *28*, 2003−2012.

(45) Aikawa, K.; Sakurai, T.; Jetter, J. J. Development of a predictive model for gasoline vehicle particulate matter emissions. *SAE Int. J. Fuels Lubr.* **2010**, *3*, 610−622.

(46) McEnally, C.; Pfefferle, L. Fuel decomposition and hydrocarbon growth processes for oxygenated hydrocarbons: butyl alcohols. *Proc. Combust Inst* **2005**, *30*, 1363−1370.

14024

dx.doi.org/10.1021/es5034316 | *Environ. Sci. Technol.* 2014, 48, 14016−14024