energy&fuels

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Cite This: Energy Fuels 2019, 33, 429−440

pubs.acs.org/EF

Investigation of the Effect of Mid- And High-Level Ethanol Blends on the Particulate and the Mobile Source Air Toxic Emissions from a Gasoline Direct Injection Flex Fuel Vehicle

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Supporting Information

ABSTRACT: This study examined the influence of low-, mid-, and high-ethanol fueling, as well as the influence of the aromatic hydrocarbons in the fuel blend, on the regulated and greenhouse gas emissions, the mobile source air toxic pollutants, and the particulate emissions from a current model flexible fuel vehicle equipped with a gasoline direct injection engine. This study utilized a total of four fuels, including a baseline U.S. EPA Tier 3 E10 fuel, one E10 fuel with higher aromatics content than the baseline E10, an E30 fuel that was splash-blended with the Tier 3 E10, and an E78 fuel. Testing was conducted over triplicate cold-start and hot-start LA92 cycles. The findings of this study showed that the higher ethanol blends, namely, the E30 and E78, led to statistically significant reductions of 9%−13% for total hydrocarbon (THC), 13%−44% for non-methane hydrocarbon (NMHC), 20%−35% for carbon monoxide (CO), and 17%−36% for nitrogen oxides (NOx) emissions compared to the high-aromatics E10 fuel. The emissions of carbon dioxide (CO_2) for the high-aromatics E10 were higher than the Tier 3 E10, E30, and E78 blends. A fuel economy penalty was also observed for lower energy content E30 and E78 blends compared to both E10 fuels. Particulate matter (PM) mass, black carbon, and total and solid particle number emissions showed statistically significant reductions for the E30 and E78 fuels compared to both E10 fuels. Results also showed that the high PM index/high-aromatics E10 produced more particulate emissions than the low PM index E10, as well as higher populations of accumulation (soot) mode particles. Acetaldehyde formation was favored by the higher ethanol content in the fuel, resulting in significant increases compared to both E10 fuels. Benzene, toluene, ethylbenzene, and xylenes (BTEX) emissions enhanced their formation with the high-aromatics E10, whereas the use of E30 and E78 fuels showed important reductions in BTEX emissions.

1. INTRODUCTION

Uses of biofuels in the United States (U.S.) and Europe have been promoted for the past several decades in an effort to reduce greenhouse gas (GHG) and other emissions from the transportation sector. Biomass-derived ethanol is the most popular biofuel in the U.S., where all gasoline sold contains up to 10% ethanol by volume (E10). Ethanol utilization is still on the rise in the U.S., with the U.S. Environmental Protection Agency (EPA) allowing 15% of ethanol by volume (E15) to be sold in the market.[1] The favorable environment for growth of ethanol fuel use is also promoted by the Energy Independence and Security Act of 2007 (EISA) and the Renewable Fuel Standard mandates. In addition to lower concentrations of gasoline−ethanol blends, gasoline is allowed to contain between 51% and 83% ethanol by volume. Higher levels of ethanol can be used in flexible fuel vehicles (FFVs), which are designed for this purpose and are certified for emissions compliance by testing with E0 and E85.

Another pathway to reduce net GHG emissions from the transportation sector and meet the federal Corporate Average Fuel Economy (CAFE) standard is to improve the engine's thermal efficiency, which will reduce fuel consumption and carbon dioxide (CO_2) emissions. Today, this technology can be achieved through the gasoline direct injection (GDI) platform that has increased in popularity in the U.S. and is expected to eventually dominate the market by replacing traditional port fuel injection (PFI) engines.[2] One of the major drawbacks of GDI technology is the exacerbated particulate matter (PM) emissions compared to PFI engines due to fuel impingement onto piston and cylinder walls. Direct injection involves the direct spray of fuel into the combustion chamber. Late evaporation of this fuel can lead to localized poor air−fuel mixing or diffusion-governed combustion that favors PM formation.[3,4]

Overall, pollutant formation is a complex function of fuel type and fuel composition, as well as combustion chemistry and physics. For example, it is expected that different fuels will produce different levels of PM emissions.[5−7] The hydrocarbon

Received: June 26, 2018
Revised: November 30, 2018
Published: December 12, 2018

DOI: 10.1021/acs.energyfuels.8b02206
Energy Fuels 2019, 33, 429−440

Table 1. Main Physicochemical Properties of the Test Fuels

property	test method	E10	E10HA	E30	E78
research octane no.	ASTM D2699	92.1	93.5	100.5	
motor octane no.	ASTM D2700	84	83.9	87.5	
octane rating		88.1	88.7	94	
sulfur content (wt %)	ASTM D5453	8	7.2	6	3
PM index (PMI)	Honda method	1.945	2.517	1.528	0.337
total aromatics (vol %)	ASTM D5769	28.1	36.7	22	5.57
C6 aromatics (benzene) (vol %)	ASTM D5769	0.599	0.565	0.457	0.168
C7 aromatics (toluene) (vol %)	ASTM D5769	7.583	9.143	5.897	1.413
C8 aromatics (vol %)	ASTM D5769	6.548	7.266	5.109	1.164
C9 aromatics (vol %)	ASTM D5769	6.124	10.229	4.808	1.794
C10+ aromatics (vol %)	ASTM D5769	5.56	7.023	4.395	0.832
olefins content	ASTM D6550	8.498	10.634	6.45	1.373
hydrogen content (wt %)	ASTM D5291	13.59	13.21	13.33	13.07
carbon content (wt %)	ASTM D5291	82.77	83.19	75.28	59.41
oxygen content (wt %)	ASTM D4815	3.63	3.59	11.39	27.52
C/H ratio		6.09	6.297	5.647	4.545
net heat of combustion (MJ/kg)	ASTM D240	41.94	41.65	38.17	30.30
density at 15.56 °C (g/cm^3)	ASTM D4052	0.7494	0.7544	0.7597	0.7830
RVP at 100 F (psi)	ASTM D5191	8.89	9.39	8.20	5.05
distillation (°C)	ASTM D86				
IBP		35	34.5	36.5	49.9
10%		51.7	53.5	57	71.1
50%		94	96.3	74.5	77.4
70%		129.1	130	78.8	77.9
90%		163.5	165.9	158.1	78.6
95%		179.1	181.8	175.7	79.4
FBP		203.5	209.1	198.8	168.2
ethanol content (vol %)	ASTM D4815	9.86	9.85	31.44	78.27

composition, especially the content and distribution of aromatics, and the distillation characteristics strongly affect PM formation.[8−10] Aikawa et al.[11] developed an empirical method called the PM index (PMI) that correlates PM emissions with the vapor pressure and the double bond equivalent (DBE) of the fuel components. Their results showed that aromatics with high boiling points and high DBE values increased PM mass and particle number emissions.

Ethanol has the potential to suppress soot formation in GDI engines and in flames.[12,13] Lemaire et al.[14] studied the effects of adding ethanol to gasoline on soot formation in turbulent spray flames and observed suppressed soot formation with ethanol, not only by dilution effect but also by chemical (oxygen) effect. Karavalakis and co-workers[15] showed reductions in PM mass, black carbon, and particle number emissions when they tested E10, E15, and E20 blends in GDI vehicles over the Federal Test Procedure (FTP) and LA92 cycles. Maricq et al.[16] documented only small reductions in PM mass and particle number emissions as the splash-blended ethanol level in gasoline increased from 0 to 20% in tests of a GDI turbocharged vehicle; however, much higher reductions in both PM mass and particle number emissions were measured for ethanol contents > 30%. Large reductions in PM mass and number emissions were also seen in a study using splash-blends of E30 and E85 on two GDI FFVs over the FTP and US06 cycles.[17] In addition to particulate emissions, previous studies on PFI and GDI FFVs have shown that an increase in ethanol content in the fuel blends reduces the emissions of nitrogen oxides (NOx), carbon monoxide (CO), non-methane hydrocarbons (NMHC), and total hydrocarbon (THC).[18,19] Hubbard et al.[20] showed reductions in THC, NO_x, and non-methane organic gases (NMOG) emissions when they tested a PFI FFV on splash-blended E20−E40 blends compared to E0. In a different study using an older technology PFI FFV with splash blends of E10, E20, E50, and E85 over the FTP, it was reported that were no statistically significant effects of CO and NO_x emissions and that THC and NMHC emission increased for E85.[21] Other studies have shown that higher ethanol concentrations can lead to elevated formaldehyde and acetaldehyde emissions, which are potentially carcinogenic compounds to humans.[22,23] Karavalakis et al.[23] reported statistically significant reductions in CO (10%−42%) and NMHC (24%−30%) emissions but sharp increases in acetaldehyde emissions (200%−260%) for E51 and E83 when they tested one FFV with a direct injection engine and one FFV with a PFI engine over the FTP and LA92 cycles. The authors found lower BTEX emissions with higher ethanol. Suarez-Bertoa et al.[24] tested a flex fuel vehicle with direct injection on E5, E10, E15, E75, and E85 blends over the New European Drive Cycle and the Worldwide harmonized Light-duty driving Test Cycle (WLTC) and found sharp increases in CO, methane (CH_4), formaldehyde, acetaldehyde, and ethanol emissions.

While there is some information available in the literature about the effects of higher ethanol blends on regulated emissions in GDI vehicles, there is limited information on the unregulated emissions, such as toxics, black carbon, and particle size distributions. The objective of this study is to investigate different ethanol concentrations, as well as the influence of higher gasoline aromatics content on emissions from a GDI FFV. This includes regulated emissions and PM mass, as well as black carbon, and particle number emissions,

DOI: 10.1021/acs.energyfuels.8b02206
Energy Fuels 2019, 33, 429−440

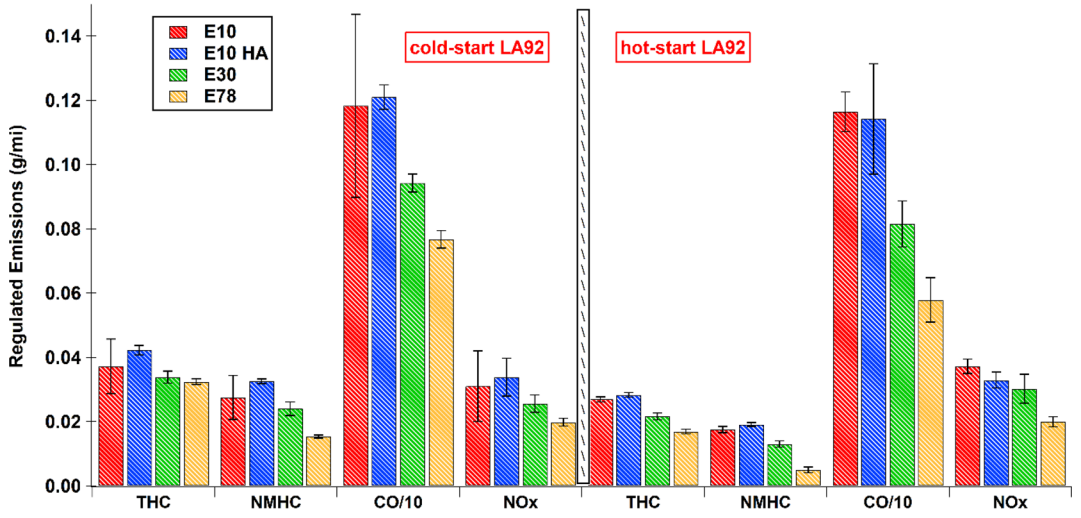

Figure 1. Regulated emissions for all test fuels over the cold-start and hot-start LA92 cycles. Data presented as mean ± standard deviation, $N = 3$.

and the mobile source air toxic pollutants. Testing was performed on a GDI flex fuel vehicle over cold-start and hot-start LA92 test cycles on a chassis dynamometer. The results of this work are discussed in the context of the impacts of ethanol concentration, aromatics content, and driving operation.

2. EXPERIMENTAL SECTION

2.1. Test Fuels and Vehicle. A total of four fuels were employed in this study, including an E10 blend with a total aromatics content of 28.1 vol %, which served as the baseline fuel. All fuels were supplied and custom blended by Gage Products Co. (Ferndale, MI, USA). While the baseline E10, hereinafter denoted as E10, was manufactured to be representative of U.S. EPA Tier 3 E10 test fuel, its total aromatics content was slightly higher than the EPA specification (21.0−25.0 vol %). For comparison purposes, this study also utilized an E10 fuel with a higher 36.7 vol % fraction of aromatics (hereinafter denoted as E10HA). Two higher ethanol blends, namely, E30 and E78, were also used to investigate the effects of higher ethanol fueling in tailpipe emissions. The E30 fuel was a splash-blend of the E10 fuel with an additional 20% ethanol. The E78 fuel was blended following the U.S. EPA Tier 3 and the California Air Recourses Board (CARB) certification requirements for E85 fuels. The blending level was selected in order to meet the ASTM D5798 Reid vapor pressure (RVP) requirement. The main properties of the test fuels are given in Table 1.

Testing was conducted on a 2016 model year FFV passenger car with a 2.0 L in-line, four-cylinder spark ignition, direct injection, wall-guided engine. The engine had a rated horsepower of 160 hp at 6500 rpm, a torque of 198 N m at 4450 rpm, and a compression ratio of 12.0 to 1. The vehicle was equipped with a three-way catalyst (TWC), was flexible fuel capable, and was certified under Federal Tier 2 Bin 5 emission standards. It had accumulated 22,854 miles at the beginning of the test campaign.

2.2. Driving Cycle and Measurement Protocol. The GDI FFV was exercised over triplicate cold-start and hot-start LA92 test cycles. The LA92 test cycle or the California Unified Cycle (UC) is a dynamometer driving schedule for light-duty vehicles developed by the California Air Resources Board (CARB). LA92 consists of three phases (i.e., cold-start, urban, and hot-start phases) and has a three-bag structure similar to the FTP cycle. LA92 is characterized by higher speeds, higher accelerations, fewer stops per miles, and less idle time than the FTP.

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 two LA4s along with idle periods between the testing on each fuel to condition the vehicle and ensure no carryover effects. The fuel change procedure is outlined in the Supporting Information (SI).

2.3. Emissions Testing. All tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL), on 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 standard bag measurements for THC, CO, NO_x, NMHC, and CO_2. Bag measurements were made with a Pierburg AMA-4000 bench. PM mass, volatile and solid particle numbers, particle size distributions, and black carbon emissions were also measured. PM was sampled from the CVS dilution system and collected onto 47 mm poly(tetrafluoroethylene) (PTFE) filters, following the procedures in 40 CFR 1065. Total and solid particle numbers were measured with a TSI 3776 ultrafine condensation particle counter (CPC) with a 2.5 nm cut point and a TSI 3776 CPC downstream from a catalytic stripper. Particle size distributions were obtained using a TSI 3090 engine exhaust particle sizer (EEPS) spectrometer. Real-time black carbon emissions were measured using an AVL micro-soot sensor (MSS). Detailed information on the methods used to collect and analyze these emissions is provided in the SI.

Samples for carbonyl analysis were collected onto 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA, USA). A Sierra mass flow controller (MFC) controlled the flow to 1.0 L/min through the cartridge. Analysis of DNPH cartridges for 14 C_1−C_8 carbonyl compounds was performed at the Organic Analytical Laboratory of the Desert Research Institute and is described elsewhere.[25] Briefly, DNPH cartridges were eluted with 2 mL of acetonitrile (HPLC grade, EMD Millipore Corp., Billerica, MA, USA) and analyzed with an HPLC system (Waters 2690 Alliance System with 996 photodiode array detector) following a modified U.S. EPA TO-11A method.[26] The HPLC response was calibrated with a certified calibration mixture purchased from AccuStandard Inc. (New Haven, CT, USA).

Hydrocarbon species were collected using a 6 L specially prepared SUMMA passivated canister, which was connected to the CVS system. Analysis of the hydrocarbon species was conducted using a gas chromatography/mass spectrometry/flame ionization detector (GC/MS/FID) analytical system with the EPA/600-R-98/161 protocol.[26]

3. RESULTS AND DISCUSSION

The following section shows the emissions results for the FFV tested on each fuel over the LA92 based on the average of all tests conducted on that particular fuel. The error bars

DOI: 10.1021/acs.energyfuels.8b02206
Energy Fuels 2019, 33, 429−440

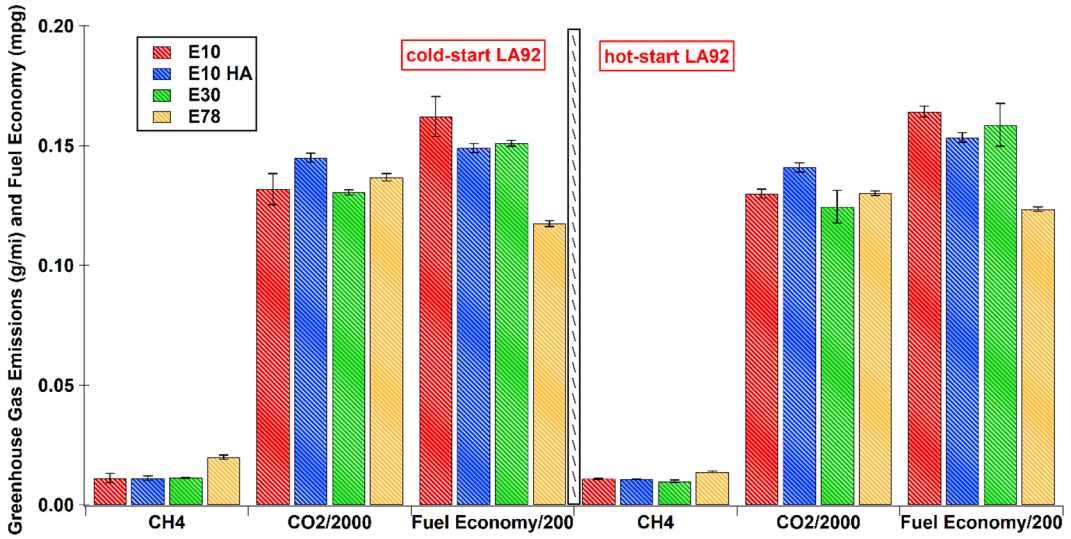

Figure 2. Greenhouse gas emissions of CO_2 and CH_4 and carbon balanced fuel economy over the cold-start and hot-start LA92 cycles. Data presented as mean ± standard deviation, $N = 3$.

represent the standard deviation for the average of each fuel. Statistical analyses were performed using a two-tailed, two-sample, equal-variance *t*-test. For the purpose of this discussion, results are considered to be statistically significant for p values ≤ 0.05 and marginally statistically significant for $0.05 \leq p < 0.1$.

3.1. Regulated Emissions. Figure 1 shows the cold-start and hot-start regulated emissions over the LA92 test cycle on the different test fuels. For the cold-start emissions, THC and NMHC followed the same patterns, with E30 and E78 blends being lower than E10 and E10HA. The higher ethanol blends did not show any statistically significant differences in THC and NMHC emissions compared to the baseline E10, whereas both E30 and E78 showed statistically significant reductions in THC emissions of 20% and 23.1%, respectively, compared to E10HA. The hot-start THC and NMHC emissions followed the same trends as those found for the cold-start LA92, but at lower concentrations. The reductions in hot-start THC and NMHC emissions for E30 and E78 blends were statistically significant compared to both E10 and E10HA fuels. Fuel E10HA showed marginally statistically significant higher hot-start THC and NMHC emissions than E10. The lower THC and NMHC emissions with higher ethanol blends were primarily due to the higher oxygen content in the ethanol, which likely increased the local oxygen in the fuel-rich regions leading to more complete combustion.[27,28] Ethanol also has a lower molecular weight compared to gasoline, so it is possible that ethanol requires less time for complete atomization and vaporization, resulting in a more homogeneous air−fuel mixture.[29] Consistent with previous studies, our results showed trends of higher THC and NMHC emissions for the higher aromatics E10 fuel.[10,30,31] Overall, aromatic hydrocarbons are more difficult to oxidize and vaporize than simpler molecules, such as alkanes or ethanol, resulting in more fuel wetting in the cylinder walls and thus higher THC emissions.[3,4,8]

For the cold-start LA92, the E30 and E78 showed statistically significant reductions in CO emissions compared to E10HA, while only the E78 fuel showed statistically significant reductions in CO emissions compared to E10. For the hot-start LA92, CO emissions for E30 and E78 blends showed statistically significant reductions compared to both E10 fuels. Cold-start and hot-start LA92 CO emissions did not show any differences between the two E10 fuels. The reduction in CO emissions with the higher ethanol blends may be attributed to the fact that ethanol has less carbon than gasoline as a consequence of the higher oxygen content in the fuel blend, which improves the oxidation of CO in the fuel-rich regions of the combustion chamber, ensuring more efficient combustion.[32]

For both cold-start and hot-start LA92 cycles, NO_x emissions decreased with an increase in ethanol content. For the cold-start LA92, E30 and E78 showed reductions in NO_x emissions at a statistically significant level compared to E10HA. Although no differences in NO_x emissions were seen between the E10 fuels for the cold-start LA92, a marginally statistically significant increase of 12% for E10 compared to E10HA was observed over the hot-start LA92. For the hot-start LA92, NO_x emissions for E78 were lower at a statistically significant level than both E10 fuels. Previous studies have shown NO_x reductions with higher ethanol blends.[22,33] Other studies have also shown higher NO_x with increasing aromatics, consistent with the differences seen between E10 and E10HA.[34] The lower NO_x emissions for the higher ethanol fuels could be due to the lower adiabatic temperature for oxygenated fuels. In addition, higher ethanol blends have a higher latent heat of vaporization and lower heating value, which can lead to a reduction in the local temperature of the air−fuel mixture at the end of the injection compared to lower ethanol blends, affecting the formation of thermal NO.[35,36]

The CO_2 emissions followed similar patterns for both the cold-start and hot-start LA92 cycles, as shown in Figure 2. The E10HA fuel showed higher CO_2 emissions at a statistically significant level compared to E10, E30, and E78. Compared to E10HA, fuels E10, E30, and E78 showed CO_2 reductions of 9%, 10%, and 6%, respectively. The higher CO_2 emissions for the E78 fuel relative to E30 was due to the higher oxygen content in the E78 blend, which improved the combustion. As expected, the influence of higher aromatics content for E10HA led to more CO_2 emissions than E10 because of the higher carbon/hydrogen ratio for this fuel. This finding is in agreement with previous studies.[10,31]

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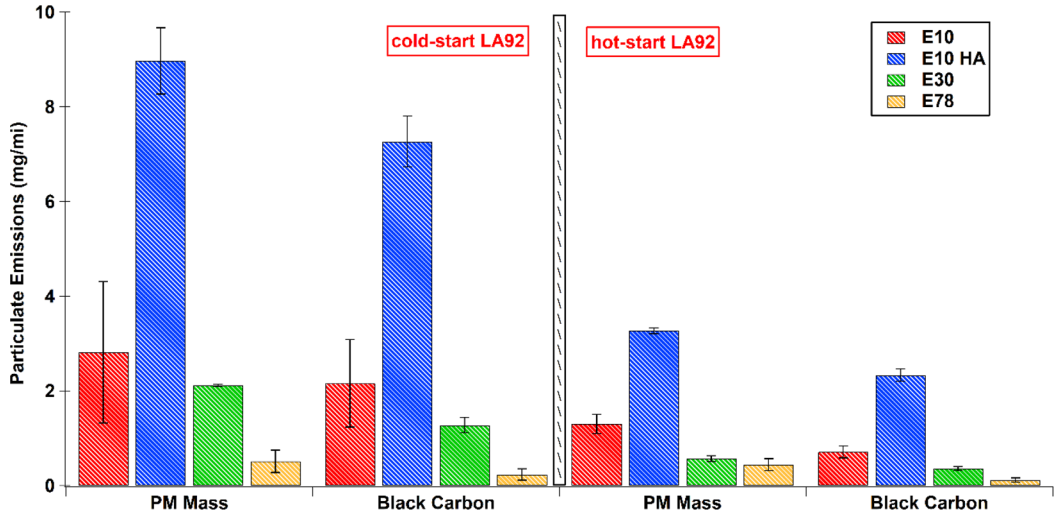

Figure 3. PM mass and black carbon emissions. Data presented as mean ± standard deviation, $N = 3$.

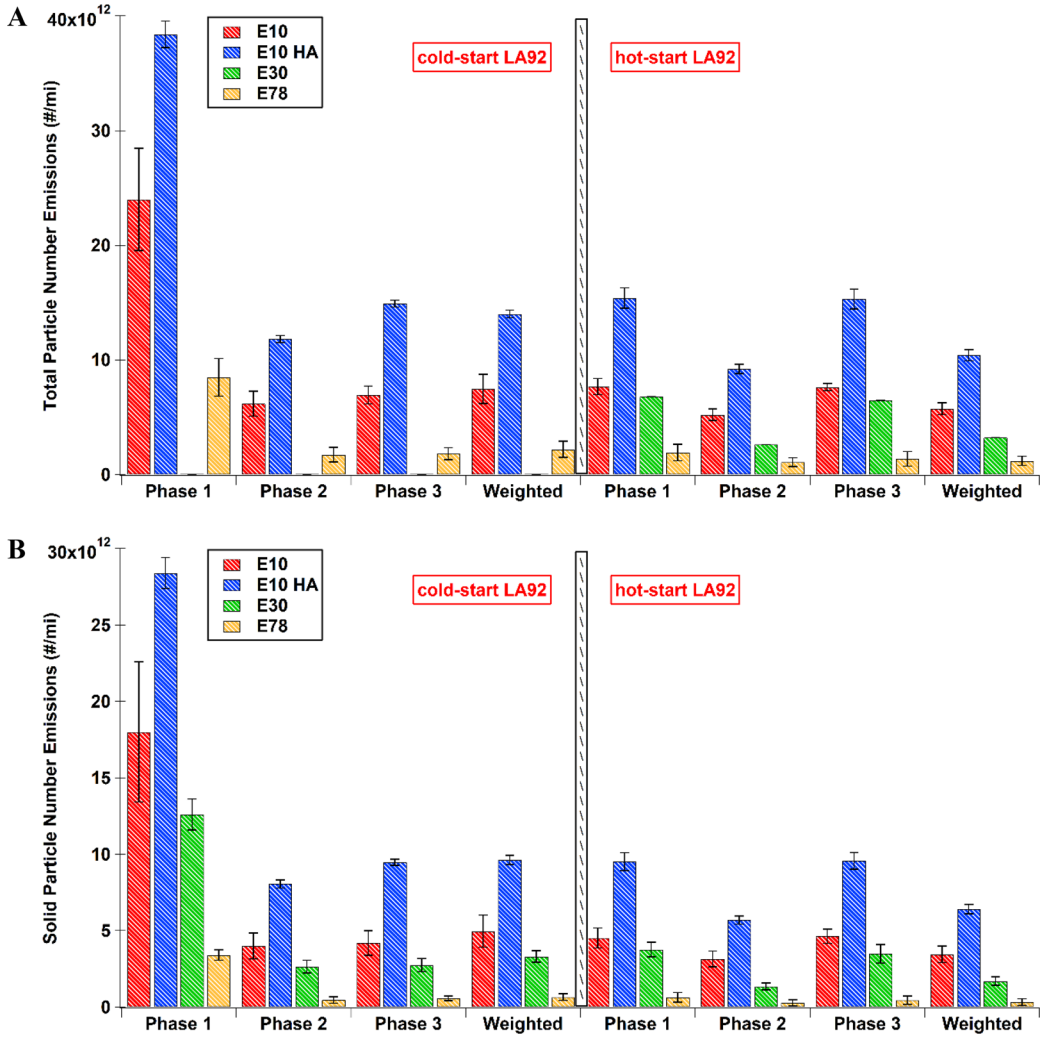

Figure 4. Total (a) and solid particle (b) number emissions over both the weighted cold-start and hot-start LA92s and their individual phases.

Emissions of CH_4 did not show any differences between the fuels for either the cold-start LA92 or the hot-start LA92, with the exception of the E78 fuel (Figure 2). Tailpipe CH_4 emissions for the E78 showed statistically significant increases compared to all the other test fuels for both cycles. More CH_4 emissions for high ethanol blends have been observed in previous studies with FFVs.[20,22] CH_4 emissions are particularly difficult to oxidize in the TWC and are primarily formed during the cold-start when the catalyst is below its light-off temperature.[37] CH_4 is also formed from the decomposition of

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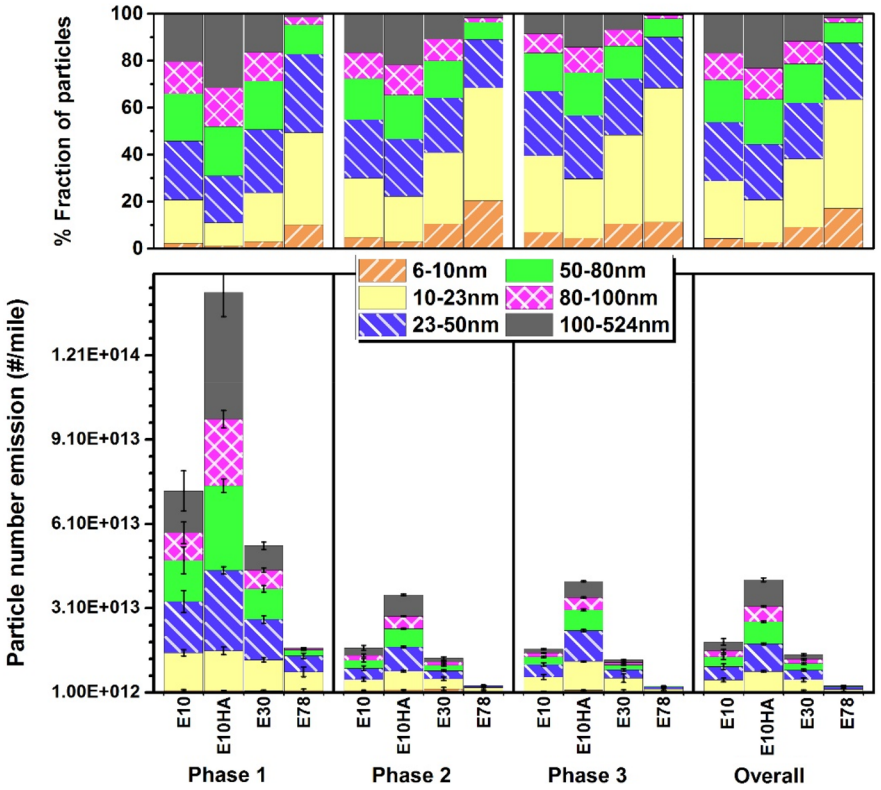

Figure 5. Particle size distribution profile and particle size fractions for the test fuels over the entire cold-start LA92 cycle and its individual phases.

acetaldehyde over rhodium (Rh)-doped TWCs,[38] with higher ethanol blends known to produce more acetaldehyde emissions.[19−21,23] Sharma et al.[39] showed a high concentration of water in the exhaust with engines operating with high ethanol blends. This layer of water can physically block the water insoluble hydrocarbons, such as CH_4, from condensing with the catalytically active sites, leading to increased emissions of CH_4.

Fuel economy was calculated based on the carbon balance method and the unique properties for each different test fuel. The results showed statistically significant reductions in fuel economy with E30 and E78 blends and for the E10HA compared to the E10 blend (Figure 2). The reductions in fuel economy were 8% for E30, 15% for E78, and 8% for E10HA over the cold-start LA92. Similar reductions in fuel economy for the high ethanol blends and the E10HA fuel were seen over the hot-start LA92, ranging from 4% to 12%. The lower fuel economy for the E30 and E78 blends was attributed to the lower energy content per gallon for these fuels compared to the E10 fuels.

3.2. PM Mass, Black Carbon, Particle Number, and Particle Size Distributions. Figure 3 shows the PM mass and black carbon emissions over the cold-start and hot-start LA92 cycles. Our results are in line with previous studies, showing that PM mass and black carbon emissions were higher over cold-start conditions due to the fact that a high fraction of these pollutants is emitted during the early phases of the cycle when the engine is cold and fuel injection results in inhomogeneous mixing between air and fuel into the combustion cylinder.[5,40] For both the cold-start and hot-start LA92 cycles, the use of higher ethanol led to large decreases in PM mass emissions compared to the E10 fuels, with E78 showing the lowest PM mass concentrations at 0.51 mg/mile. Compared to E10 fuel, cold-start and hot-start LA92 PM mass for E30 and E78 showed reductions in the ranges of 25%−56% and 66%−82%. For the cold-start LA92, the higher PMI E10HA fuel (PMI = 2.517) produced higher PM mass than the other fuels and a statistically significant increase of 218% relative to the lower PMI E10 (PMI = 1.945). The E30 (PMI = 1.528) and E78 (PMI = 0.337) blends showed statistically significant reductions in PM mass of 76% and 94%, respectively, compared to E10HA. For the hot-start LA92, the E30 and E78 blends showed statistically significant reductions in PM mass emissions compared to both the high and low PMI E10 fuels. The high-PMI E10 exhibited 151% higher PM mass than the low-PMI E10 at a statistically significant level.

Analogous to the PM mass, black carbon emissions showed large reductions with E30 and E78 blends compared to both E10 fuels. For the cold-start LA92, black carbon emissions showed statistically significant reductions of 82% and 92% for E30 and E78, respectively, compared to the high PMI E10HA fuel. The difference between the high-PMI E10HA and the low-PMI E10 in black carbon emissions was 70% at a statistically significant level. Similar statistically significant reductions in black carbon emissions were also seen for the hot-start LA92 for the high ethanol blends compared to the E10 fuels, and for E10HA compared to E10.

Total and solid particle number emissions are shown in Figure 4a,b. It should be noted that total particle number measurements were not made for E30 over the cold-start LA92 due to instrument failure. Fuel type and composition had particularly strong impacts on both the total and solid particle number emissions, with statistically significant reductions for the E30 and E78 blends compared to the E10 fuels and statistically significant increases for the higher PMI E10HA

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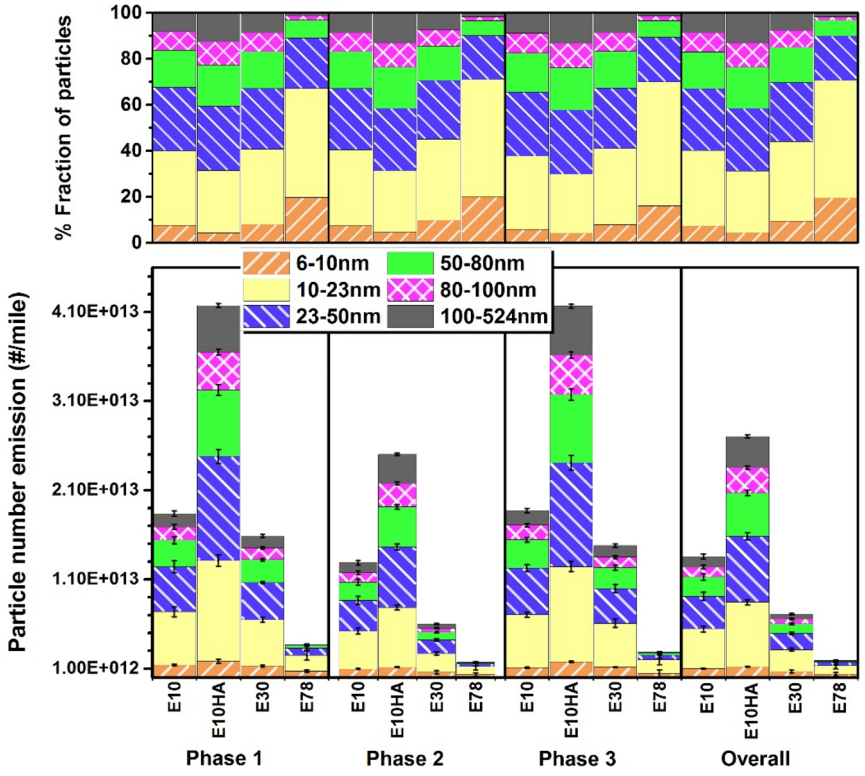

Figure 6. Particle size distribution profile for the test fuels over the entire hot-start LA92 cycle and its individual phases.

relative to the low-PMI E10. For the cold-start LA92, the reductions in total and solid particle number emissions compared to the high-PMI E10 ranged from 47%−84% and from 49%−93%, respectively. For the hot-start LA92, these reductions ranged from 45%−89% and from 46%−95%, respectively. The cold-start phase (bag 1) of the LA92 dominated the formation of both total and solid particle number emissions. During the cold-start phase of the LA92, the cold engine with its cold walls and components make fuel evaporation much more difficult. Because the TWC is below its light-off temperature, more fuel is introduced in the cold combustion chamber to heat the catalyst resulting in mixture inhomogeneity and diffusive combustion from fuel pools.[3] For the hot-running (bag 2) and hot-start (bag 3) phases, total and solid particle number emissions were found in lower concentrations than in bag 1. Higher fuel temperatures and piston surface temperatures promote better fuel vaporization and a more homogeneous air−fuel mixture.[41]

Overall, our results are in agreement with the majority of the published literature showing a positive effect of ethanol on particulate emissions from GDI engines.[15,16,42,43] The reductions in particulate emissions with E30 and E78 fuels were likely due to dilution effects, resulting from aromatic content reduction in the fuel, as opposed to the increased oxygen content of ethanol that enhanced soot oxidation. Aromatics and polyaromatics have a higher sooting tendency than nonaromatic hydrocarbons.[44] Diluting the aromatics in the fuel stream for the higher ethanol blends will lower the soot precursor formation and reduce the soot surface growth through the HACA (hydrogen abstraction acetylene addition) mechanism.[13,45]

As previously discussed, aromatics content and fuel volatility had a strong influence on particulate emissions for the two E10 fuels. The high PMI E10HA fuel had a higher content of total aromatics than the lower PMI E10 and contained higher concentrations of compounds with high boiling points and DBE values. The higher the boiling point and DBE of the aromatic species in the fuel, the more particulate emissions increase. This is also reflected to the strong correlations between the PMI and PM mass emissions for both LA92 cycles. Due to the higher boiling points of aromatic hydrocarbons, they are more difficult to vaporize during combustion compared to other hydrocarbons (alkanes and olefins) or oxygenates (i.e., ethanol) because aromatics burn at higher adiabatic flame temperatures. In addition, the distillation temperatures of T90 and T95 are higher for the E10HA fuel relative to E10, indicating that this fuel contains more of heavier hydrocarbon fractions that are more difficult to evaporate. This will likely result in a poor air−fuel mixture and diffusion combustion (pool fire) of liquid fuel, leading to higher soot emissions. Previous studies have also shown increased particulate emissions with higher aromatic content gasoline fuels.[5,8−10,46,47]

Figure 5 and Figure 6 illustrate the particle size distribution characteristics for all test fuels over the cold-start and hot-start LA92s, respectively. For most fuels, the particle size distributions showed bimodal profiles, consisting of a nucleation mode (10−23 nm) and an accumulation mode (23−100 nm). For all test fuels and both cycles, the nucleation mode was centered at around 15 nm, whereas the accumulation mode was centered at 70−80 nm. The cold-start LA92 produced much higher particle populations in the accumulation mode but not in the nucleation mode. This suggests that fuel-rich combustion during cold-start conditions contributes to the formation and growth of soot particles in the accumulation mode.[41,48] For both LA92 cycles, the E30 and E78 fuels showed reductions of accumulation mode particles compared to E10, with these reductions for the cold-start

DOI: 10.1021/acs.energyfuels.8b02206
Energy Fuels 2019, 33, 429−440

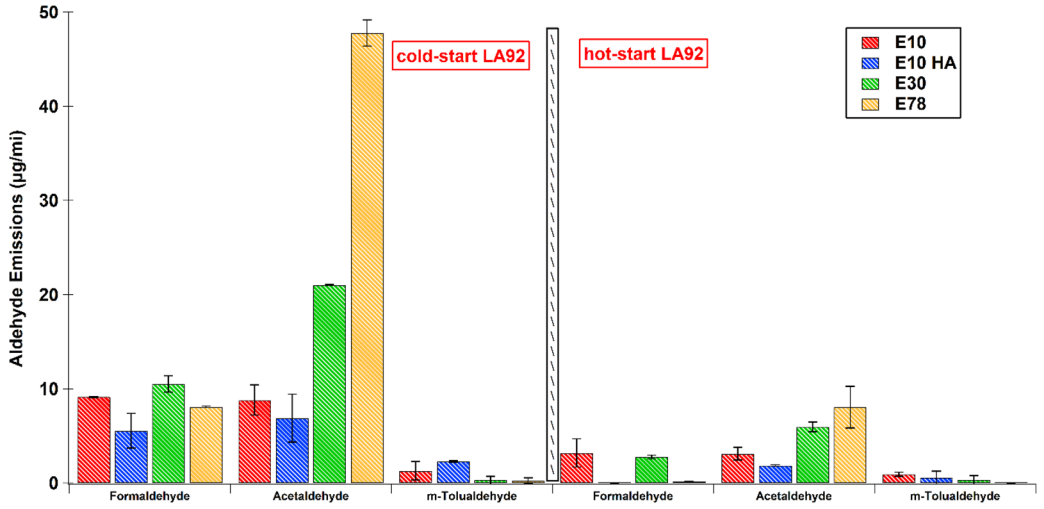

Figure 7. Aldehyde emissions over the cold-start and hot-start LA92 cycles.

LA92 being 29.7% and 88.6% for E30 and for the hot-start LA92 at 50.5% and 92.3% for E78, respectively. The high PMI E10HA fuel showed increases in the accumulation mode particles compared to E10 on the order of 123.2% and 116.8%, respectively for the cold-start and hot-start LA92s. The use of E30 and E78 produced reductions in nucleation mode particles with respect to E10 of 9.3% and 66.1% for the cold-start LA92 and at 44.7% and 78% for the hot-start LA92, respectively. For the E78 fuel, the soot mode was practically eliminated, with the nucleation mode particles dominating the particle size distribution profile at 46% over the cold-start LA92 and at 51% over the hot-start LA92. Our findings are consistent with previous studies showing that, with increasing alcohol content, peak particle number concentrations and particle size are decreased.[29,42,49] It is worth noting that the particle size distribution profile for the hot-running and hot-start segments for both the cold-start and hot-start LA92 cycles were very similar, with the main differences in particle sizing observed for the cold-start segment or bag 1 for both cycles.

The increased oxygen content, which suppresses soot formation, and, more importantly, the dilution of aromatics in the fuel lower the rates of soot precursor formation and thus the accumulation mode particles.[50] It is theorized that ethanol slows down the coagulation process leading to soot by reducing the formation of polycyclic aromatic hydrocarbons, which are precursors to soot particles. It is important to note that, for both driving cycles, the E30 and E78 fuels exhibited higher concentrations of nucleation mode particles and a lower formation of soot particles, suggesting the high ethanol blends primarily contributed to nucleation mode particles via the available soot surface area on which hydrocarbons adsorb or condense, favoring nucleation. The sooting tendency of E10HA was considerably higher than that for the low PMI E10 fuel, which can be ascribed to the higher aromatics content of this fuel. The particle size distributions of E10HA were dominated by the accumulation soot mode over both cycles, ranging at 56.2% for the cold-start LA92 and 55.7% for the hot-start LA92. These findings are in agreement with the higher PM mass and black carbon emissions for the higher PMI E10HA fuel relative to the lower PMI E10.

3.3. Aldehyde Emissions. Figure 7 shows the aldehyde emissions for both the cold-start and hot-start LA92 cycles. Formaldehyde and acetaldehyde were the most dominant aldehydes in the exhaust followed by *m*-tolualdehyde. Previous studies have also shown that formaldehyde and acetaldehyde emissions are the principal aldehydes from ethanol exhaust.[22−24,51] The concentrations of aldehyde emissions were found to be significantly higher over the cold-start LA92 compared to the hot-start LA92 cycle. This result was as expected, since aldehydes emissions are primarily formed during the initial part of the cycles (bag 1) when the TWC is below its light-off temperature. The impact of ethanol was particularly strong in acetaldehyde emissions, with E30 and E78 showing higher acetaldehyde emissions at a statistically significant level compared to both E10 fuels. For the cold-start LA92, the increases in acetaldehyde emissions for E30 and E78 were 206% and 595% compared to E10HA and 139% and 443% compared to E10. For the hot-start LA92, acetaldehyde emissions increased by 222% for E30 and 335% for E78 relative to E10HA, and by 92% for E30 and 158% for E78 relative to E10. Acetaldehyde emissions did not show any statistically significant effects between the two E10 fuels. These observations are in agreement with other studies and a building consensus that acetaldehyde is produced from the partial oxidation of ethanol.[23,43,52] Ethanol combustion will result in hydrogen abstraction, which will form radicals that react with either oxygen or unimolecularly decompose yielding acetaldehyde.[53]

Formaldehyde emissions showed statistically significant effects for some fuels but not for others. For the cold-start LA92, E30 showed a marginally statistically significant increase in formaldehyde emissions of 47% compared to E10HA, whereas E78 showed a statistically significant reduction in formaldehyde emissions of 12% compared to E10. E10HA trended lower for formaldehyde emissions than E10, but these differences were not statistically significant. A reduction in aromatics could lead to lower formaldehyde and acetaldehyde emissions because these compounds do not participate in their formation pathways.[52,54] Formaldehyde could be formed from the breakdown of the C−C bond in the initial step of ethanol combustion. Both increases[22,43] and decreases[55] in formaldehyde emissions with higher ethanol blends have been reported in previous studies. Emissions of the aromatic *m*-tolualdehyde also showed strong and statistically significant reductions for E30 (87%) and E78 (90%) compared to E10HA, but not compared to E10. The addition of oxygen and

DOI: 10.1021/acs.energyfuels.8b02206
Energy Fuels 2019, 33, 429−440

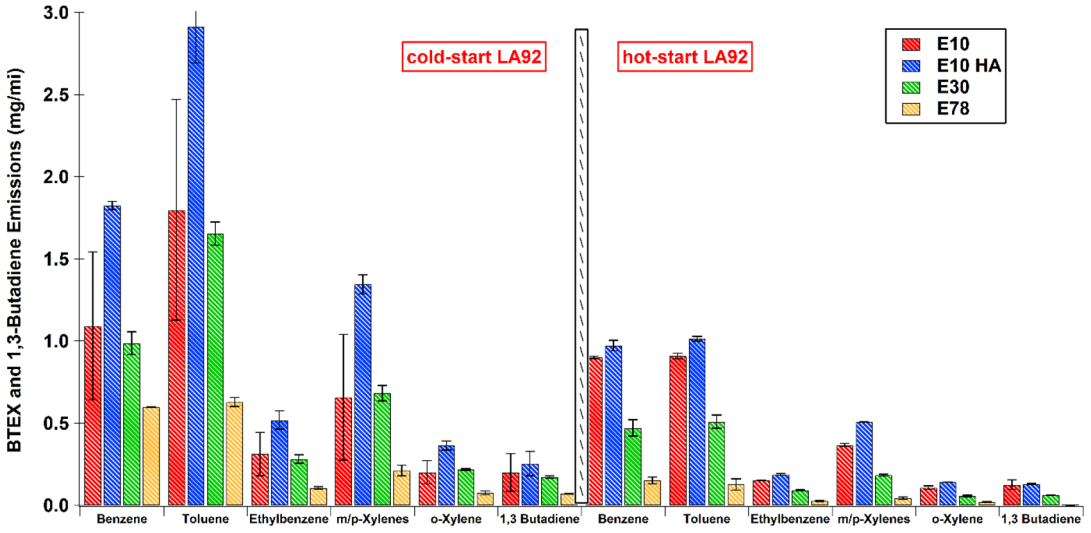

Figure 8. BTEX (benzene, toluene, ethylbenzene, and xylenes) and 1,3-butadiene emissions over the cold-start and hot-start LA92 cycles.

the lower content of aromatics in the fuel, such as *m*-/*p*-xylenes, yielded lower *m*-tolualdehyde emissions.

3.4. Monoaromatic and VOC Emissions. The monoaromatic hydrocarbons of benzene, toluene, ethylbenzene, *m*-/*p*-xylenes, and *o*-xylene (collectively known as BTEX), as well as 1,3-butadiene, are shown in Figure 8. Other volatile organic compounds (VOCs) measured over both driving cycles are shown in SI Table S1. For the cold-start LA92, the use of E30 and E78 fuels resulted in large and statistically significant reductions in BTEX emissions compared to E10HA, but not always compared to E10 fuel. In most cases, BTEX levels for E30 were similar to those of E10, possibly indicating that the intermediate E30 blend caused regions locally rich in aromatics and thus slower evaporation of heavier aromatic species, which in turn resulted in BTEX emissions similar to those of E10 over the cold-start LA92.[56] This phenomenon may potentially explain the small differences in THC and PM mass emissions between the E10 and E30 fuels. The E78 blend showed the lowest BTEX emissions compared to both E10 fuels over both driving cycles. Compared to E10HA, the statistically significant reductions in BTEX emissions for E30 ranged from 40% to 49% and for E78 ranged from 67% to 84%. The lower BTEX emissions for E30 and E78 blends were largely due to the lower aromatics content in these fuels, as opposed to the fuel-bound oxygen assisting the hydrocarbon oxidation process. E10HA trended higher for BTEX emissions compared to E10, but not at a statistically significant level. Previous studies have also shown lower BTEX emissions with ethanol fuels in gasoline engines.[43,51] For 1,3-butadiene emissions, the only statistically significant reduction was seen for E78 (72%) relative to E10HA. Generally, 1,3-butadiene is produced by the partial combustion of olefins in the fuel and it has been reported that it decreases its concentrations with oxygenates.[37] The E10HA fuel had the highest total olefins levels and E78 the lowest among the test fuels. It has also been reported that cyclohexane (higher concentration in E10HA than E78) is a major compound that participates in the formation of 1,3-butadiene.[54]

BTEX and 1,3-butadiene emissions were found in lower concentrations over the hot-start LA92 compared to the cold-start LA92. The warm engine and catalyst better facilitate the oxidation of these species. Emissions of 1,3-butadiene for E78 were below the detection limit of the method, while the 1,3-butadiene emissions for E30 were statistically significantly lower than both E10 fuels. It should be noted that the impacts of fuel aromatics and oxygen content were stronger during the hot-start LA92 than the cold-start conditions. During the cold-start LA92, fuel volatility contributed to the formation of monoaromatic emissions, especially for the fuels with higher T90 and T95 distillation temperatures. It is possible that partially unburned heavier fuel fractions escaped the cold catalyst forming BTEX emissions. In addition, the cold-start period of the cycle appeared to negatively influence the variability of some pollutants, an effect that is not obvious for the hot-start LA92. For the hot-start LA92, BTEX emissions for the E30 and E78 blends showed statistically significant reductions compared to both E10 fuels. For all BTEX species, E10HA was statistically significantly higher compared to E10 fuel. The benzene, toluene, ethylbenzene, and xylenes contents were higher for the high- compared to low-aromatic fuels, indicating that these emissions were closely related to the content of aromatics in the fuel. The benzene levels for the two E10 fuels, however, were about the same, suggesting that benzene is formed by the dealkylation of toluene and xylenes during combustion (methyl group for toluene and xylene and ethyl group for ethylbenzene).[57] Cyclohexane is also a precursor for benzene formation,[58] and the use of ethanol has been shown to decrease benzene formation.[37,43]

Ethylene and acetylene are important hydrocarbon precursors due to their ability to form soot via the HACA mechanism.[59] Both ethylene and acetylene were higher for E10HA and E78 fuels. Both pollutants can be produced during combustion from C_2 radicals formed through H-abstractions and β-scissions and from fuel aromatics. While ethanol usually decreases the formation of these pollutants, more ethylene and acetylene emissions were seen for E78 fuel. Ethylene may be produced from the dehydration of ethanol above 160 °C.[43] This finding is not in agreement with the very low PM mass and black carbon emissions for the E78 fuel compared to the other fuels. Ethane emissions trended higher for E10HA and E78. Ethane formation is enhanced by cyclohexane, but it also appears that ethanol is oxidized to ethane. Propylene emissions decreased with E30 and E78, with E10HA showing the highest propylene concentrations. The compounds *n*-pentane and

DOI: 10.1021/acs.energyfuels.8b02206
Energy Fuels 2019, 33, 429−440

2,2,4-trimethylpentane (isooctane) were found in relatively high concentrations for all test fuels, and their emission levels were primarily dependent on the concentrations in the fuel. Isopentane and 1-butene were found in high concentrations for the E10 fuels and the E30 blends, but in low levels for E78. The formations of isopentane and 1-butene were mainly enhanced by isooctane, where both E10 fuels and the E30 had higher levels than E78.[58] The compounds 1-hexene and *n*-hexane were also detected in higher levels for the two E10 fuels and E30 compared to E78. Both species are exclusively enhanced from unburned fuel components.[60] Several mono-aromatic species, such as *m*-ethyltoluene, *p*-ethyltoluene, *o*-ethyltoluene, 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene were detected in lower concentrations than the BTEX species. The use of E78 decreased their emissions, with the E10HA fuel showing higher concentrations of these pollutants.

4. CONCLUSIONS

This study evaluated the gaseous and particulate emissions from a FFV equipped with a wall-guided direct injection gasoline engine. Testing was conducted over cold-start and hot-start LA92 cycles when the vehicle was operated on two E10 fuels with different levels of aromatic hydrocarbons and an E30 and an E78 blend. Our results showed that the use of higher ethanol blends resulted in lower THC, NMHC, CO, and NO_x emissions from a current technology GDI FFV. The higher aromatics E10 fuel showed higher THC and NMHC emissions than the lower aromatic E10 fuel, suggesting the formation of these pollutants was more sensitive to fuel aromatics than CO and NO_x emissions. The GHG emissions of CO_2 showed some increases for E78 compared to E10, while CH_4 emissions significantly increased for the E78 blend compared to the other fuels. This could potentially be a concern for high-concentration ethanol blends considering the global warming potential for both the CO_2 and CH_4 gases. As expected, the vehicle experienced a fuel economy penalty with the higher ethanol blends due to their lower energy content per gallon compared to the E10 fuels.

The results reported in this study also demonstrated strong PM mass, black carbon, AND total and solid particle number emissions reductions with the higher ethanol blends and the lower PMI E10 fuel compared to the high-PMI E10HA. The higher PMI fuel led to increased populations of accumulation mode particles, with the E78 blend having an almost unimodal particle distribution dominated by nucleation mode particles. Ethanol fuels showed a clear increase in acetaldehyde emissions but mixed results for formaldehyde emissions. The fuel effect on BTEX and 1,3-butadiene emissions was particularly strong, with aromatics being the main driver for their formation. Fuels with lower aromatics and higher ethanol contents showed lower BTEX and 1,3-butadiene emissions. Overall, this study provides valuable insights on the impacts of ethanol content and gasoline composition on the exhaust emissions from a current technology GDI FFV.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b02206.

Additional details about fuel change protocol and emissions analysis (PDF)

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge funding from the South Coast Air Quality Management District (SCAQMD) under Contract 15625 and ICM Inc. under Contract 16070832. We thank Mr. Mark Villela and Mr. Daniel Gomez of the University of California, Riverside for their contribution in conducting the emissions testing for this program.

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