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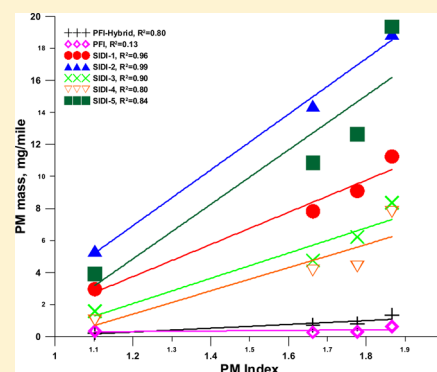
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S Supporting Information

ABSTRACT: We assessed the emissions response of a fleet of seven light-duty gasoline vehicles for gasoline fuel aromatic content while operating over the LA92 driving cycle. The test fleet consisted of model year 2012 vehicles equipped with spark-ignition (SI) and either port fuel injection (PFI) or direct injection (DI) technology. Three gasoline fuels were blended to meet a range of total aromatics targets (15%, 25%, and 35% by volume) while holding other fuel properties relatively constant within specified ranges, and a fourth fuel was formulated to meet a 35% by volume total aromatics target but with a higher octane number. Our results showed statistically significant increases in carbon monoxide, nonmethane hydrocarbon, particulate matter (PM) mass, particle number, and black carbon emissions with increasing aromatics content for all seven vehicles tested. Only one vehicle showed a statistically significant increase in total hydrocarbon emissions. The monoaromatic hydrocarbon species that were evaluated showed increases with increasing aromatic content in the fuel. Changes in fuel composition had no statistically significant effect on the emissions of nitrogen oxides (NO_x), formaldehyde, or acetaldehyde. A good correlation was also found between the PM index and PM mass and number emissions for all vehicle/fuel combinations with the total aromatics group being a significant contributor to the total PM index followed by naphthalenes and indenes.



INTRODUCTION

Today, gasoline is the most widely used automotive fuel in the U.S. transport sector, accounting for over 65% of total transportation energy consumption.¹ Gasoline is blended from a number of refinery streams such that the final properties meet specifications established by regulatory or standards organizations. On a molecular level, each of these streams and the final blend can be viewed as a composition of hundreds of hydrocarbons, which themselves can be divided into four classes of compounds: paraffins, olefins, cycloparaffins, and aromatics. Gasoline may also contain oxygenates, such as alcohols and ethers. Commercial gasoline may be dosed with several additives in the part per million (ppm) concentration range to prevent fuel degradation (i.e., antioxidants) or improve engine performance (i.e., detergents).² The exact relationship between gasoline formulation and air quality has been a challenge for regulatory environmental agencies, automotive manufacturers, and the fuel industry, even though it is known that gasoline fuel composition is directly linked to engine emissions.^{3–5} Several extensive studies have been conducted to investigate the impact of gasoline composition on tailpipe emissions. These include, for example, the Auto/Oil Air Quality Improvement Research Program (AQIRP) performed in the early 1990s as well as studies by the US Environmental

Protection Agency (EPA).^{6–8} More recent studies have been carried out to evaluate the effect of oxygenates (ethanol) on gasoline volatility and exhaust emissions, and the influence of varying olefin content on exhaust emissions.^{9,10}

All of this research led to a better understanding of the relationship between gasoline formulations and emissions and contributed to the development of the so-called “complex model” to estimate nitrogen oxides (NO_x), volatile organic compounds (VOCs), and toxic emissions as a function of fuel properties to support compliance with the federal reformulated gasoline (RFG) program.^{11,12} One of the avenues available for compliance with the RFG performance standards has been to lower the aromatic content of gasoline as the complex model indicates that lowering aromatic content can reduce emissions. Gasoline aromatics have been reduced over the past decade at the national level with their reduction being a challenge to refiners because refinery streams rich in aromatics were a traditional source of high octane molecules. Today, refiners have replaced some of the octane value of aromatic streams

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with oxygenates, like ethanol, in addition to other changes. Adding oxygenates does allow the aromatic content to be reduced. It should be noted that although there is no limit for gasoline aromatics on a federal level, California has set limits for RFG phase 3 of 25% and 0.80% by volume for aromatics and benzene, respectively.

Aromatic hydrocarbons are unsaturated compounds with a benzene ringlike structure and are known to form polycyclic aromatic hydrocarbons (PAHs), which are precursors of soot particles.^{13,14} Several studies have shown an increase in particulate matter (PM) emissions with increasing aromatics content in gasoline.^{8,15–18} Other studies have also reported that gasoline vehicles are a major contributor of secondary organic aerosol (SOA) formation and that aromatics in gasoline are largely responsible for its PM formation potential.¹⁹ A recent study has shown an estimate of ~3800 predicted premature mortalities nationwide originating from aromatic hydrocarbons in gasoline and a total social cost of \$28.2 billion.²⁰

Currently, there is limited information concerning the effect of gasoline composition on emissions from vehicles equipped with emerging spark ignition (SI) engine technologies. Although port fuel injection (PFI) is the prevalent technology in current production light-duty vehicles, the desire for higher fuel efficiency and lower greenhouse gas emissions has led to increased use of SI direct injection (SIDI) engines in the US market. In the US alone, the penetration of SIDI vehicles has increased from 4% in 2009 to 38% in 2014.²¹ However, SIDI engines are known to emit more PM mass and particle number (PN) than conventional PFI engines.^{22,23} The increase in particulate emissions is mostly due to the fact that less time is available for fuel vaporization and mixture preparation to occur in the SIDI operation relative to that of the PFI operation, which leads to greater charge heterogeneity and liquid fuel impingement onto the piston and cylinder surfaces.²⁴

A number of epidemiological and toxicological studies have shown that nanoparticles have more adverse health effects than micron-sized particles.²⁵ Recently, concerns about the health and environmental effects of nanoparticles have pushed the European Union to introduce a PN standard, limiting the number of nonvolatile particles emitted from SIDI vehicles over the certification New European Driving Cycle (NEDC) to 6.0×10^{12} particles/km in 2014 and 6.0×10^{11} particles/km in 2017. Although the US has not implemented a PN limit for SIDI vehicles, it has adopted a federal PM mass FTP standard of 3 mg/mile for light-duty vehicles beginning with model year 2017 that is stricter than that in Europe (5 mg/km). Furthermore, California has promulgated a 1 mg/mile standard for light-duty vehicles beginning with model year 2025.²⁶ Therefore, a study of the effect of gasoline fuel composition on gaseous emissions and, especially, particulate emissions from SIDI vehicles is of significant importance.

The US EPA recently conducted a comprehensive study of the effects of gasoline fuel properties on exhaust emissions and included an evaluation of gasoline aromatics content, but its efforts were limited to only PFI vehicles.⁸ Previous studies evaluating the impact of aromatics content on emissions dates back to the early 1990s.^{18,27,28} The purpose of this study is to evaluate the impact of changes in gasoline's total aromatics content on tailpipe emissions from a fleet of modern technology PFI and SIDI vehicles. Emission measurements were conducted on seven vehicles (including two with PFI fueling and five with DI fueling) during cold-start and transient operation over the LA92 driving cycle. Each vehicle was tested

on four different gasoline fuels with varying aromatic contents. The emissions results are discussed in the context of changing gasoline fuel composition and engine technology.

■ EXPERIMENTAL SECTION

Test Fuels and Vehicles. Four fuels were employed in this study, all supplied and custom blended by Gage Products Company (Ferndale, MI). The fuel test matrix included three gasolines blended to meet nominal total aromatics targets of 15% (denoted fuel A), 25% (denoted fuel B), and 35% (denoted fuel C) by volume. A fourth fuel (denoted fuel D) had the same total aromatics content as fuel C but was blended to meet a target Anti-Knock Index (AKI) value that was higher by at least 3 octane numbers. For comparison, the minimum and maximum AKIs, research octane numbers (RONs), and motor octane numbers (MONs) for fuels A, B, and C ranged from 87.1 to 87.8, 90.4 to 92.0, and 82.8 to 84.5, respectively, whereas fuel D had an AKI, RON, and MON of 91.2, 96.6, and 85.7, respectively. The higher octane rating for fuel D was obtained through a higher volume of isoparaffins at 26.2% compared to the 21.1% by volume for fuel C and, specifically, an ~7.5% increase in isooctane for fuel D. The main physicochemical properties of the test fuels are provided in the Supporting Information (SI), Table S1. Additional detailed hydrocarbon analysis for the test fuels and the analytical measurement method are given in the SI, Table S2.

This study utilized seven 2012 model year light-duty vehicles, as shown in the SI, Table S3. The test matrix included one hybrid vehicle with PFI fueling (PFI-Hybrid), one conventional PFI passenger car (PFI), and five light-duty vehicles with DI fueling and wall-guided fuel injection systems (SIDI-1 to SIDI-5). All vehicles operated stoichiometrically and had three-way catalysts (TWCs). Six of the vehicles were certified to meet either the Federal Tier 2, Bin 2 emission standards or the California LEV-II, SULEV emission standards. SIDI-5, a light-duty truck, was certified to meet Tier 2 Bin 4 emission standards.

Driving Cycles and Measurement Protocol. Each vehicle/fuel combination was tested using the LA92 test cycle or the California Unified Cycle (UC), which is a dynamometer driving schedule for light-duty vehicles developed by the California Air Resources Board (CARB). The LA92 consists of three phases (i.e., cold-start, urban, and hot-start phases) and has a similar three-bag structure to the Federal Test Procedure (FTP) cycle. The LA92 is characterized by higher speeds, higher accelerations, fewer stops per miles, and less idle time than the FTP.

At least two replicates were performed for each vehicle/fuel combination. A third test was performed if the difference in the measurements recorded during the first two tests exceeded the following: 33% total hydrocarbons (THC), 29% NO_x, and 70% carbon monoxide (CO), provided that the absolute difference in the measurements was greater than 5 mg/mile.^{9,10,29} Before the first test, each vehicle was preconditioned with a procedure that included multiple drains and fills, a catalyst sulfur purge cycle, and coast downs on the dynamometer. More details on the preconditioning procedure for the conventional vehicles and hybrid vehicle are provided in the SI.

Emissions Testing and Analysis. 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 certifica-

tion-quality emissions measurements. For all tests, standard bag measurements were obtained for THC, CO, NO_x, nonmethane hydrocarbon (NMHC), and carbon dioxide (CO₂). Bag measurements were made with a Pierburg AMA-4000 bench. Carbonyl compounds and 1,3-butadiene, benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, PM mass, PN, and black carbon emissions were also measured. Detailed information on the methods used to collect and analyze these compounds is provided in the SI.

RESULTS AND DISCUSSION

Statistical analyses of each of the pollutants were performed using the Mixed procedure in PC/SAS from the SAS Institute, Inc. A more detailed description of the statistical analysis is provided in the SI. The statistical analyses of fuel effects grouped the six Tier 2 Bin 2 and SULEV-certified vehicles separately from the Tier 2 Bin 4 vehicle. The weighted THC, NO_x, and CO₂ emission and fuel economy results are presented in Table 1. Summaries of statistical comparisons of the effects associated with the different fuels are provided separately for the Tier 2 Bin 2 and SULEV vehicle groups and the Tier 2 Bin 4 vehicle in Tables S4 and S5, respectively, in the SI. Emission results for the individual phases of the LA92 cycle are provided in Table S6 in the SI.

Regulated Emissions and Fuel Economy. The weighted THC emissions from the six Tier 2 Bin 2 and SULEV vehicles did not show any statistically significant differences between fuels. On the other hand, the THC emissions from the SIDI-5 vehicle increased with increasing fuel aromatic content and decreased with higher octane number when comparing the two fuels with high total aromatics (fuels C and D). For the SIDI-5 vehicle, THC emissions for fuel C showed statistically significant increases of 48%, 17%, and 21% relative to fuels A, B, and D, respectively, and fuel B showed statistically significant higher THC emissions of 28% compared to fuel A. The fuel trends for THC emissions for the individual LA92 phases were not as strong with only the cold-start phase for the SIDI-5 vehicle showing a statistically significant increase of 47% for fuel C compared to fuel A and a marginally statistically significant increase of 29% for fuel B compared to A.

Weighted NMHC emissions exhibited strong fuel effects based on comparisons of the different fuel pairs, as shown in Figure 1a and Tables S4 and S5 in the SI. For the Tier 2 Bin 2 and SULEV vehicles, weighted NMHC emissions for fuel C showed statistically significant increases of 23% and 27% compared to fuels A and B, respectively. For the SIDI-5 vehicle, fuel C showed statistically significant increases in NMHC emissions of 61% and 21% compared to fuels A and B, respectively, and a marginally statistically significant increase of 19% compared to fuel D. Fuel B also showed 33% higher weighted NMHC emissions relative to fuel A at a statistically significant level. For the cold-start phase, the Tier 2 Bin 2 and SULEV vehicles showed NMHC emissions for fuel C that were increased by 44% and 33% compared to fuels A and B, respectively. For the SIDI-5 vehicle, fuel C showed 58% statistically significant higher NMHC emissions than fuel A, and fuel B showed 34% marginally statistically significant higher NMHC emissions than fuel A.

Previous studies have shown increases in both THC and NMHC emissions with increasing aromatics content in gasoline.^{7,18,30–33} In general, aromatics are more difficult to vaporize than paraffins, so the amount of fuel trapped on metal surfaces and in cylinder deposits should be greater with higher

Table 1. Weighted Regulated Emissions and Carbon Balance Fuel Economy for All Vehicles/Fuel Combinations over the LA92 Cycle^a

vehicle	fuel A		fuel B		fuel C		fuel D		fuel A		fuel B		fuel C		fuel D	
	THC Weighted (g/mile)	CO ₂ Weighted (g/mile)	THC Weighted (g/mile)	CO ₂ Weighted (g/mile)	THC Weighted (g/mile)	CO ₂ Weighted (g/mile)	THC Weighted (g/mile)	CO ₂ Weighted (g/mile)	NO _x Weighted (g/mile)	Fuel Economy Weighted (miles/gal)	NO _x Weighted (g/mile)	Fuel Economy Weighted (miles/gal)	NO _x Weighted (g/mile)	Fuel Economy Weighted (miles/gal)	NO _x Weighted (g/mile)	Fuel Economy Weighted (miles/gal)
PFI-Hybrid	0.0038 ± 0.0014	201.1 ± 5.1	0.0032 ± 0.0019	203.1 ± 4.2	0.0046 ± 0.0007	202.4 ± 3.5	0.0023 ± 0.0005	199.4 ± 0.2	0.0094 ± 0.0015	41.6 ± 1.05	0.0100 ± 0.0020	42.6 ± 0.88	0.0071 ± 0.0008	44.0 ± 0.75	0.0092 ± 0.0002	44.4 ± 0.06
PFI	0.0069 ± 0.0033	314.9 ± 2.3	0.0058 ± 0.0003	323.5 ± 6.2	0.0090 ± 0.0017	331.0 ± 1.8	0.0072 ± 0.0005	325.6 ± 1.8	0.0197 ± 0.0082	26.3 ± 0.23	0.0208 ± 0.0052	26.6 ± 0.51	0.0161 ± 0.0031	26.7 ± 0.17	0.0191 ± 0.0025	27.0 ± 0.14
SIDI-1	0.0045 ± 0.0008	313.3 ± 2.4	0.0043 ± 0.0005	318.8 ± 3.3	0.0045 ± 0.0007	322.3 ± 2.2	0.0060 ± 0.0011	330.4 ± 8.1	0.0094 ± 0.0009	26.7 ± 0.20	0.0093 ± 0.0008	27.2 ± 0.27	0.0098 ± 0.0006	27.6 ± 0.19	0.0115 ± 0.0007	26.8 ± 0.67
SIDI-2	0.0061 ± 0.0023	392.8 ± 2.9	0.0044 ± 0.0003	405.9 ± 0.2	0.0062 ± 0.0002	410.7 ± 0.1	0.0050 ± 0.0002	409.6 ± 4.3	0.0059 ± 0.0003	21.2 ± 0.16	0.0063 ± 0.0002	21.3 ± 0.00	0.0060 ± 0.0008	21.6 ± 0.01	0.0061 ± 0.0002	21.6 ± 0.23
SIDI-3	0.0053 ± 0.0008	389.5 ± 3.6	0.0068 ± 0.0006	400.3 ± 3.0	0.0069 ± 0.0016	404.7 ± 3.7	0.0056 ± 0.0000	407.4 ± 5.1	0.0070 ± 0.0004	21.5 ± 0.20	0.0072 ± 0.0013	21.6 ± 0.16	0.0072 ± 0.0013	22.0 ± 0.20	0.0073 ± 0.0005	21.7 ± 0.27
SIDI-4	0.0062 ± 0.0001	284.9 ± 3.2	0.0078 ± 0.0005	289.9 ± 2.2	0.0061 ± 0.0014	296.0 ± 4.9	0.0075 ± 0.0008	296.2 ± 1.5	0.0101 ± 0.0016	29.2 ± 0.35	0.0074 ± 0.0019	29.7 ± 0.23	0.0110 ± 0.0032	29.9 ± 0.50	0.0072 ± 0.0031	29.7 ± 0.14
SIDI-5	0.0180 ± 0.0011	530.9 ± 2.2	0.0231 ± 0.0007	541.5 ± 7.2	0.0269 ± 0.0019	557.4 ± 2.9	0.0222 ± 0.0006	541.4 ± 5.3	0.0069 ± 0.0012	15.7 ± 0.1	0.0048 ± 0.0007	16.0 ± 0.2	0.0053 ± 0.0014	16.0 ± 0.1	0.0059 ± 0.0013	16.3 ± 0.2

^aThe ± error bars represent one standard deviation of the average values for the individual vehicles.

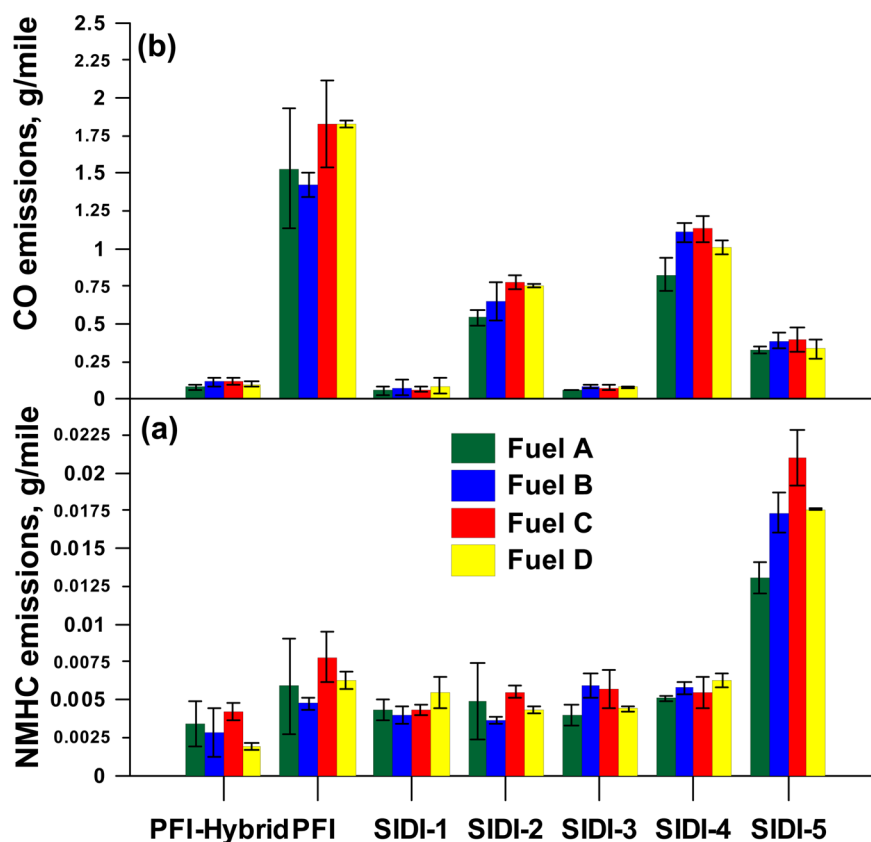


Figure 1. NMHC (a) and CO emissions (b) for all vehicle/fuel combinations over the LA92 cycle. The error bars represent one standard deviation of the average values.

aromatic fuels.³⁴ Our results are partly in line with a recent EPA study of Tier 2 compliant vehicles with PFI fueling showing that both NMHC and THC emissions increased with increasing gasoline aromatics content during both cold-start and hot-running conditions with the aromatics effect being greater for NMHC than for THC emissions.⁸ These results suggest that improvements in emissions controls for the latest technology vehicles may reduce fuel impacts on THC/NMHC emissions compared to those for older vehicles.⁷

Weighted CO emissions are presented in Figure 1b for each of the individual test vehicles. For the group of Tier 2 Bin 2 and SULEV vehicles, weighted CO emissions showed a statistically significant increase of 26% for fuel B compared to fuel A and of 33% for fuel C compared to fuel A. For the cold-start phase, the results showed a statistically significant increase of 33% for fuel C compared to fuel B and of 44% for fuel C compared to fuel A. For the SIDI-5 vehicle, CO emissions did not show as strong of a fuel effect with the only statistically significant or marginally statistically significant differences seen for the hot-start phase for fuels B and C compared to A. Overall, increases in CO emissions with increasing aromatics content have been seen in previous studies.^{7,8,18,35} The lower CO emissions for fuels A and B may also be a consequence of the lower 50% distillation temperature (T50) compared to fuel C.⁹ Although fuel D had a similar T50 temperature to those of fuels A and B, there were other factors that also clearly affected CO emissions, such as the higher aromatics content.

NO_x emissions generally did not show any statistical significant fuel effects for either the Tier 2 Bin 2 and SULEV vehicles or the SIDI-5 vehicle. Our results agree with previous studies performed on SIDI vehicles showing no statistically

significant effects for NO_x with higher aromatics fuels.³⁶ Our results also suggest that aromatic content will not have as strong an effect on NO_x emissions for modern technology vehicles as compared to older technology vehicles, although the literature does not necessarily show consistent trends between fuel aromatics content and NO_x emissions.^{8,33} A number of studies of older PFI vehicles have shown decreases in tailpipe NO_x emissions with increasing aromatics, somewhat in contrast to what might be expected from fundamental combustion.^{7,18,34,35} From a fundamental combustion standpoint, aromatic hydrocarbons have higher combustion and peak flame temperatures than alkanes and paraffinic fuels, which could contribute to higher engine-out NO_x emissions.³⁷

CO₂ emissions show a slight, but statistically significant, upward trend with increasing levels of aromatics. This trend was seen for all of the Tier 2 Bin 2 and SULEV vehicles except for the PFI-Hybrid. Upon evaluation of CO₂ for the Tier 2 Bin 2 and SULEV vehicles as a group, this trend was statistically significant for: (1) the weighted, cold-start, and hot-running CO₂ emissions when comparing fuels B versus A, C versus B, and C versus A, and (2) the hot-start phase when comparing fuels B versus C and A versus C. For the SIDI-5 vehicle, CO₂ emissions also showed increases with higher aromatic fuels. A reduction in CO₂ for the higher octane level was also found for SIDI-5, which could be due to more efficient combustion relative to fuel C. The increase in CO₂ emissions for fuel C can be attributed to the higher carbon content per unit energy for fuel C compared to fuels A and B, and the percentage differences in CO₂ emissions between fuels A, B, and C correspond closely to the differences in percent differences seen in the carbon content per unit energy for these fuels. Increasing

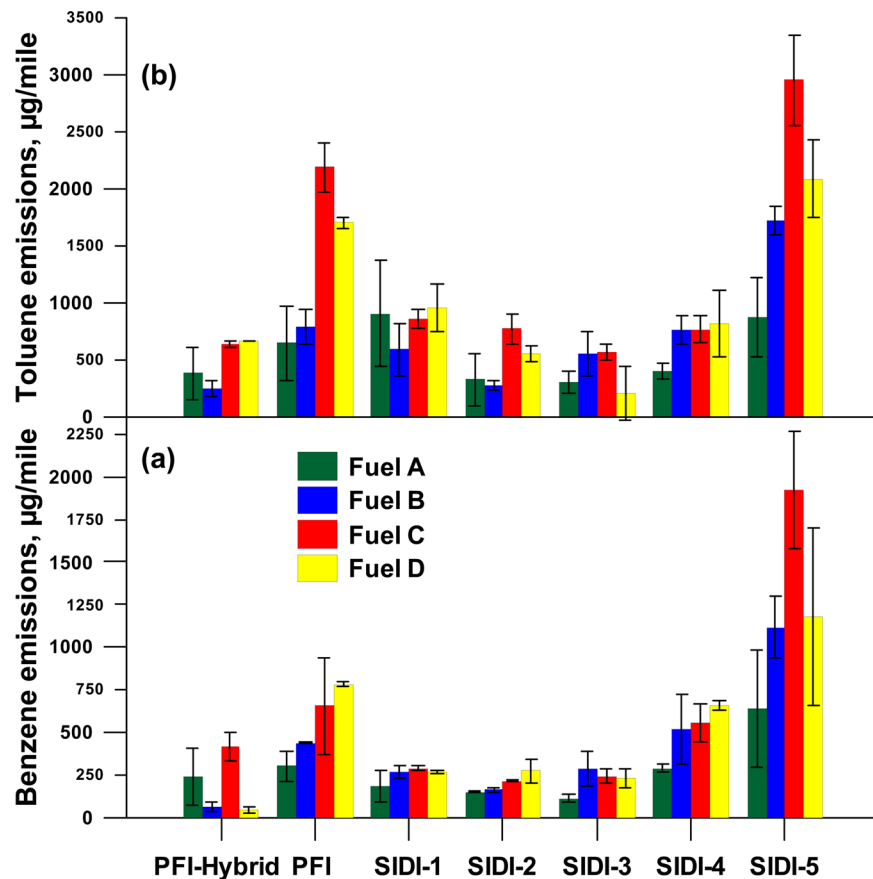


Figure 2. Benzene (a) and toluene (b) emissions for all vehicle/fuel combinations over the LA92 cycle. The error bars represent one standard deviation of the average values.

Table 2. Gaseous Toxic Pollutants for All Vehicles/Fuel Combinations over the LA92 Cycle^a

vehicle	fuel A	fuel B	fuel C	fuel D	fuel A	fuel B	fuel C	fuel D
	1,3-Butadiene (µg/mile)				Ethylbenzene (µg/mile)			
PFI-Hybrid	9.3 ± 5.9	0.0 ± 0.0	9.0 ± NA	0.0 ± 0.0	31.0 ± 28.5	18.7 ± 4.2	70.1 ± 13.5	34.1 ± 38.6
PFI	12.0 ± 4.3	11.3 ± 13.7	19.0 ± 22.1	20.0 ± 9.1	43.8 ± 58.7	71.3 ± 7.2	185.2 ± 6.7	158.1 ± 10.6
SIDI-1	12.9 ± NA	15.0 ± 2.5	14.2 ± 12.2	26.2 ± NA	183.8 ± 127.7	79.5 ± 33.8	124.0 ± 16.2	143.1 ± 18.8
SIDI-2	6.9 ± 9.8	18.2 ± 23.0	14.7 ± 16.0	3.7 ± 5.2	36.3 ± 12.3	37.3 ± 10.9	110.7 ± 26.8	100.0 ± 11.0
SIDI-3	1.0 ± 1.4	30.3 ± 0.6	3.9 ± 5.6	0.0 ± 0.0	46.2 ± 4.9	75.3 ± 32.1	83.1 ± 6.4	139.9 ± NA
SIDI-4	20.8 ± 1.1	5.2 ± 6.6	14.3 ± 0.5	7.9 ± 6.9	53.5 ± 18.6	123.7 ± 9.4	115.4 ± 20.4	160.3 ± 47.7
SIDI-5	51.4 ± 59.4	93.7 ± 19.6	66.2 ± 43.3	57.9 ± 14.2	133.7 ± 25.0	203.0 ± 4.0	403.2 ± 76.8	107.1 ± 1.6
	<i>m/p</i> -Xylene (µg/mile)				<i>o</i> -Xylene (µg/mile)			
PFI-Hybrid	24.0 ± 21.0	22.6 ± 32.0	255.4 ± 125.4	69.8 ± 98.7	7.6 ± 12.8	5.4 ± 7.7	62.8 ± 30.4	15.6 ± 22.1
PFI	119.8 ± 104.8	292.2 ± 43.9	783.4 ± 171.1	811.9 ± 18.3	19.2 ± 27.1	60.9 ± 0.2	144.2 ± 31.4	126.1 ± 47.4
SIDI-1	311.1 ± 254.9	185.4 ± 64.4	327.5 ± 44.2	273.5 ± 105.2	85.0 ± 69.3	40.8 ± 21.6	101.4 ± 30.9	62.1 ± 25.5
SIDI-2	94.4 ± 21.0	96.7 ± 10.1	335.7 ± 102.6	300.2 ± 40.3	25.9 ± 8.1	26.8 ± 2.3	84.7 ± 28.5	91.5 ± 3.8
SIDI-3	93.3 ± 6.4	203.4 ± 74.3	212.6 ± 16.3	382.1 ± NA	25.0 ± 4.3	44.7 ± 21.7	53.1 ± 3.4	78.3 ± NA
SIDI-4	118.5 ± 48.4	357.7 ± 4.0	364.7 ± 81.9	538.4 ± 53.2	28.9 ± 9.0	93.2 ± 2.4	93.8 ± 22.7	126.3 ± 15.6
SIDI-5	311.6 ± 60.7	576.4 ± 104.9	1336.4 ± 140.8	572.2 ± 98.3	97.5 ± 23.0	163.8 ± 30.3	343.3 ± 58.5	153.2 ± 40.6
	Formaldehyde (µg/mile)				Acetaldehyde (µg/mile)			
PFI-Hybrid	24.9 ± 43.2	34.1 ± 48.2	8.0 ± 11.3	0.0 ± 0.0	363.0 ± 220.5	130.5 ± 171.4	244.9 ± 97.8	133.7 ± 43.6
PFI	171.4 ± 118.9	316.4 ± 189.9	151.6 ± 177.7	316.5 ± 31.6	320.5 ± 55.4	346.9 ± 137.4	379.9 ± 206.9	359.4 ± 63.3
SIDI-1	252.6 ± 219.3	150.3 ± 74.9	57.7 ± 48.6	121.1 ± 52.9	283.7 ± 186.4	305.3 ± 68.6	225.3 ± 143.4	194.7 ± 35.4
SIDI-2	0.0 ± 0.0	0.0 ± 0.0	33.6 ± 47.5	106.1 ± 150.0	118.4 ± 48.4	73.0 ± 33.8	139.3 ± 36.8	220.3 ± 174.7
SIDI-3	70.7 ± 35.0	93.0 ± 131.5	226.1 ± 287.8	166.6 ± 54.7	166.8 ± 111.0	247.1 ± 113.9	271.1 ± 126.8	202.3 ± 10.5
SIDI-4	0.0 ± NA	63.9 ± 76.4	3.4 ± 4.9	9.0 ± 15.0	91.3 ± NA	182.4 ± 51.2	156.6 ± 97.1	124.1 ± 81.1
SIDI-5	475.5 ± 147.2	598.7 ± 24.2	412.2 ± 258.4	706.7 ± 144.1	605.5 ± 129.0	434.1 ± 57.4	426.9 ± 110.8	620.0 ± 77.3

^aThe ± error bars represent one standard deviation of the average values for the individual vehicles.

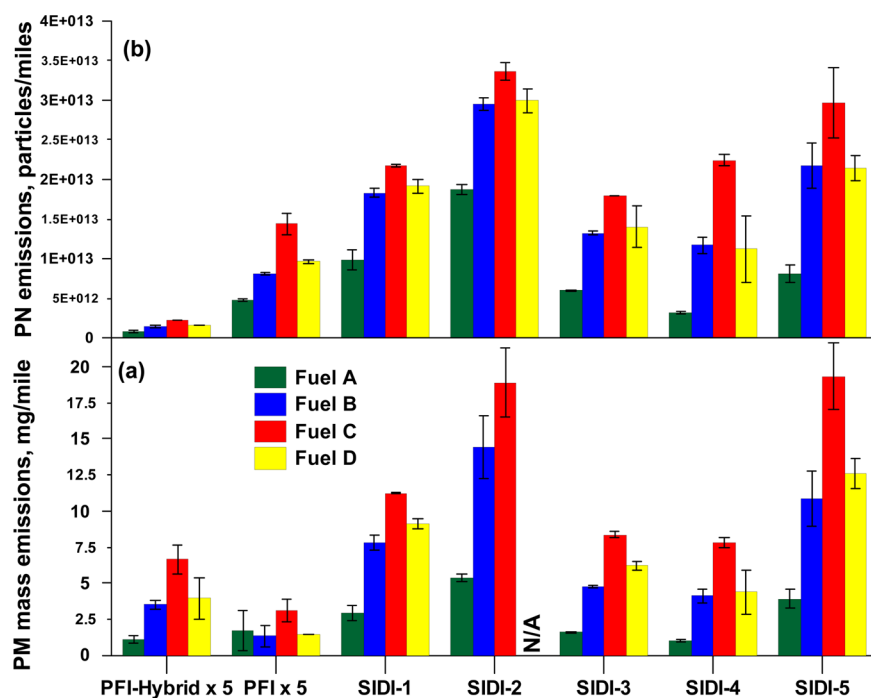


Figure 3. PM mass (a) and PN (b) emissions for all vehicle/fuel combinations over the LA92 cycle. Note that PM mass and PN emissions for the PFI-Hybrid and PFI vehicles are multiplied by a factor of 5. The error bars represent one standard deviation of the average values.

the aromatics content of a gasoline usually results in an increase in the carbon/hydrogen ratio, leading to an increase in CO_2 emissions. This result is consistent with previous studies.¹⁸

Fuel economy was calculated based on the carbon balance method and the unique properties of each different fuel. For the six Tier 2 Bin 2 and SULEV vehicles, fuel economy showed increases with increasing aromatics for all three LA92 phases and the weighted values, which were statistically significant in most cases. For the weighted fuel economy, fuel B showed a 1.3% increase compared to fuel A, and fuel C showed increases of 1.3% and 2.6% compared to fuels B and A, respectively. For the SIDI-5 vehicle, the improvements in fuel economy were not as consistent as for the other six vehicles. For the weighted fuel economy, only fuel D showed a statistically significant increase of 2.3% compared to fuel C. The increases in fuel economy with the higher aromatic fuels can be attributed to the higher energy content of these fuels compared to fuel A.

BTEX and 1,3-Butadiene Emissions. Figure 2(a,b) shows the benzene and toluene emissions, respectively, and Table 2 summarizes the emissions of 1,3-butadiene, ethylbenzene, *m/p*-xylenes, and *o*-xylene for the entire fleet of seven vehicles for samples collected cumulatively for each test. For all vehicle/fuel combinations, toluene was the most dominant monoaromatic compound in the exhaust followed by benzene, xylenes, and ethylbenzene. Overall, emissions of these monoaromatic compounds increased with increasing aromatic content in the fuel. For the Tier 2 Bin 2 and SULEV vehicles, statistically significant increases were seen for BTEX emissions for most fuel pairs, ranging from 52% to 103% for fuel B compared to fuel A, from 81% to 194% for fuel C compared to fuel B, and from 107% to 376% for fuel C compared to fuel A. Increases in these aromatic species for fuel C compared to the higher octane fuel D ranged from 127% to 272%. For the SIDI-5 vehicle, statistically significant increases were also seen for BTEX species emissions for most fuel pairs, ranging from 53% to 103% for fuel B compared to fuel A, from 71% to 133% for fuel

C compared to fuel B, and from 201% to 333% for fuel C compared to fuel A. Increases in BTEX species for fuel C compared to the higher octane fuel D ranged from 127% to 272%. It is expected that the BTEX species would increase with increasing total aromatics as well as higher contents for individual species in the fuels, as BTEX species can be formed from unburned fuel or partially burned heavier aromatics with some contribution derived from other hydrocarbons. The benzene content was held constant in the test fuels, whereas toluene and xylenes increased from the low to high aromatics gasolines. This phenomenon indicates that substantially more benzene emissions were produced when toluene, xylenes, and ethylbenzene were present in the fuel, as opposed to unburned benzene, whereas the other BTEX species could be formed from higher aromatic species or via unburned fuel that escapes the emission control system before the catalyst reaches its light-off temperature. It is likely that benzene was produced primarily by the dealkylation of toluene and xylenes during combustion (methyl group for toluene and xylene, and ethyl group for ethylbenzene).³⁸ Dealkylation also may occur across the catalyst.³⁴

Emissions of 1,3-butadiene did not show any statistically significant differences between fuels for either the Tier 2 Bin 2 and SULEV vehicles or the SIDI-5 vehicle. Generally, 1,3-butadiene is not present in gasoline and is formed from the partial combustion of olefins. The lack of fuel trends for the 1,3-butadiene emissions under the present test conditions could be due to the fact that olefins were held relatively constant as a fuel variable. Previous studies of older PFI vehicles have shown decreases in 1,3-butadiene emissions with increasing aromatics in gasoline, however.^{7,8,35}

Aldehyde Emissions. Formaldehyde and acetaldehyde were the most dominant aldehydes in the exhaust as shown in Table 2. Formaldehyde and acetaldehyde collected cumulatively for each test did not show any strong statistically significant effects between fuels. The results reported here

generally showed that acetaldehyde emission levels were higher than those of formaldehyde, which can be attributed to the presence of ~10% of ethanol in the test fuels. Acetaldehyde is principally formed due to the partial oxidation of ethanol via the abstraction of a secondary H atom leading to the α -hydroxyethyl radical (CH_3CHOH), which either reacts with O_2 or unimolecularly decomposes to yield a radical and acetaldehyde.³⁹ Previous studies of older vehicles have generally shown a decrease in both formaldehyde and acetaldehyde emissions with increasing aromatics content because aromatics are not major precursors to their formation.^{7,18,34,40} In contrast to earlier studies on older technology vehicles/engines, the EPA study on Tier 2 compliant gasoline vehicles showed that both formaldehyde and acetaldehyde emissions increased with increasing aromatics content in the fuel at a statistically significant level.⁸

PM Mass, Particle Number, and Black Carbon Emissions. The cycle-based PM mass emissions are depicted in Figure 3a, and PN emissions are shown in Figure 3b. PM mass for the PFI fueled vehicles ranged from 0.2 to 1.3 mg/mile, and the SIDI vehicles were approximately an order of magnitude higher, ranging from 1.0 to 19.3 mg/mile. PN emissions corroborate the PM mass emissions with the SIDI vehicles showing substantially higher PN counts than their PFI counterparts. Significantly lower PM mass and number emissions have been reported in previous chassis dynamometer studies utilizing PFI vehicles compared to SIDI vehicles.^{41,42} Higher particulate emissions from SIDI engines can be ascribed to the shorter time for mixture preparation/evaporation and homogenization, leading to liquid fuel impingement on the piston and cylinder walls.^{23,43} As a consequence, the fuel that emerges from the fuel films produces fuel-rich regions that generate high emissions of PM.

The PM mass and number emissions both showed strong, statistically significant fuel trends. The highest PM mass and number emissions were observed for fuel C, and the lowest PM mass and number emissions were seen for fuel A. Fuels B and D showed PM mass and number emissions intermediate to those for fuels A and C. For the Tier 2 Bin2 and SULEV vehicles, the increases in cumulative PM mass were 148% for fuel B compared to fuel A, 73% for fuel C compared to B, and 330% for fuel C compared to A. For the SIDI-5 vehicle, the increases in PM mass were 177% for fuel B compared to fuel A, 79% for fuel C compared to fuel B, 395% for fuel C compared to fuel A, and 53% for fuel C compared to fuel D. Particle number emissions, for the Tier 2 Bin2 and SULEV vehicles, showed increases of 94% for fuel B compared to fuel A, 41% for fuel C compared to fuel B, and 173% for fuel C compared to fuel A. Fuel C also had cumulative PM mass and weighted PN emissions that were 49% and 32% higher, respectively, than those for the higher octane fuel D. For PN emissions of the SIDI-5 vehicle, increases were 169% for fuel B compared to fuel A, 36% for fuel C compared to fuel B, 266% for fuel C compared to fuel A, and 38% for fuel C compared to fuel D.

The results reported here exhibited a strong relationship between gasoline composition and PM mass and number emissions. Several studies have also shown a strong influence of gasoline fuel properties on particulate emissions with the bulk of these studies showing higher PM emissions with increasing aromatics content in the fuel.^{15,44,45} Aromatic hydrocarbons are known precursors to soot formation.¹⁴ Soot can be produced via addition reactions and condensation of the aromatic rings into a carbonaceous structure or through slower fragmentation-

polymerization reactions. Aromatic compounds can act as seed molecules for molecular growth and polymerization to form larger hydrogen-deficient molecules (PAHs) that produce soot.^{14,47} Particulate emissions can also be correlated with higher double bond equivalent (DBE) values and higher boiling points (bp) for different chemical species in the fuel. Differences in molecular structure and DBE between paraffins and aromatic hydrocarbons contribute to greater particulate emissions for aromatics.^{46,48,49} For example, the DBEs of paraffins is 0, whereas the DBEs of aromatic hydrocarbons, depending on the molecular structure, are approximately 4 to 7. In addition, components with higher boiling points and lower corresponding vapor pressures evaporate more slowly, resulting in a greater tendency for diffusion combustion instead of premixed combustion. This results in more imperfect fuel mixing and diffusion-controlled burning of thin films of liquid fuel on the piston, leading to higher particulate emissions.

The results of this study show that the particulate mass and number increase as the boiling points of the hydrocarbons are increased. Assuming equal carbon number in the hydrocarbons, aromatics have an ~28 K higher boiling point than paraffinic species; thus, aromatics are more difficult to vaporize than paraffins. For instance, 2,2,4-trimethylpentane (isooctane) boils at 372.4 K whereas ethylbenzene boils at 410 K; therefore, higher aromatic content fuel evaporates slower, which can contribute to higher particulate emissions.⁵⁰ It is interesting to note that although fuels C and D had similar total aromatic contents, fuel D exhibited lower PM mass and number emissions than fuel C. It is theorized that the differences in PM mass and number emissions for fuels C and D can be attributed to the specific molecular structure of the constituents in the fuels. In contrast to fuel D, fuel C contained 2.4 \times more of the high molecular weight isoparaffins (C_{10} – C_{12}), 1.2 \times more aromatics (C_{10} – C_{12}), 5.6 \times more mononaphthenes (C_8 – C_{10}), and 2.0 \times more isoolefins (C_8 – C_{10}) than fuel D, which are characterized by high boiling points ranging from 415 to 473 K for the isoparaffins, 450 to 498 K for the aromatics, 382 to 455 K for the mononaphthenes, and 403 – 445 K for the isoolefins.

As discussed above, the higher the boiling point and DBE of the aromatic hydrocarbons in gasoline, the more particulate emissions increase. Compounds such as *m*-xylene (~412 K bp), toluene (~383 K bp), 1,2,4-trimethylbenzene (~442 K bp), indene (~455 K bp), and indan (~451 K bp), as well as naphthalene (~491 K bp) all have relatively high boiling points, which can contribute to increases in particulate emissions. It should be stressed that fuel C also contained heavier normal paraffins (DBEs of 0) with higher boiling points than fuel D, including those of *n*-decane (446 K bp), *n*-undecane (469 K bp), and *n*-dodecane (486 K bp), which all have similar boiling points to that of naphthalene and to higher chain aromatics. Fuel D also had a lower content of naphthalene, indene, and indan than fuel C, directionally consistent with the relationship between higher PM mass and number emissions and boiling point. It is worth noting that fuel A did not contain a measurable amount of indene and had lesser amounts of heavier aromatic hydrocarbons in the C_{11} – C_{12} range with both high DBEs (4) and boiling points (460–498 K bp).

Consistent with previous studies,^{44,46} our work further validates the relationship between gasoline composition and PM emissions using the PM Index (PMI), which is a fuel composition algorithm capable of predicting the PM emissions from gasoline composition. The PMI for each fuel was calculated according to the equation provided in Aikawa et

Table 3. PM Index for the Test Fuels and PM Indices Distribution for the Different Fuels Based on Chemical Groups

	fuel A		fuel B		fuel C		fuel D	
	wt (%)	PMI (%)	wt (%)	PMI (%)	wt (%)	PMI (%)	wt (%)	PMI (%)
total PMI		1.102		1.663		1.866		1.777
paraffin	11.084	2.311	14.638	1.462	15.568	1.611	12.765	0.678
isoparaffins	44.317	8.381	28.497	3.682	18.535	2.040	23.343	2.181
mono-aromatics	18.436	68.783	31.428	75.013	41.375	81.790	41.376	82.754
naphthalenes	0.225	7.603	0.295	6.865	0.225	4.512	0.230	4.967
naphtheno/olefino-benzenes	0.319	3.912	0.503	4.301	0.396	3.068	0.402	3.246
indenes	0.538	5.282	0.785	6.307	0.806	4.702	0.697	4.576
mono-naphthenes	5.231	1.814	5.087	1.158	5.325	1.204	3.310	0.532
<i>n</i> -olefins	6.354	0.932	6.214	0.613	5.273	0.530	6.583	0.598
isoolefins	0.793	0.344	0.761	0.155	0.747	0.140	0.521	0.076
naphtheno-olefins	0.099	0.038	0.134	0.045	0.131	0.052	0.089	0.021
oxygenates	11.032	0.601	10.504	0.400	10.276	0.352	10.422	0.374

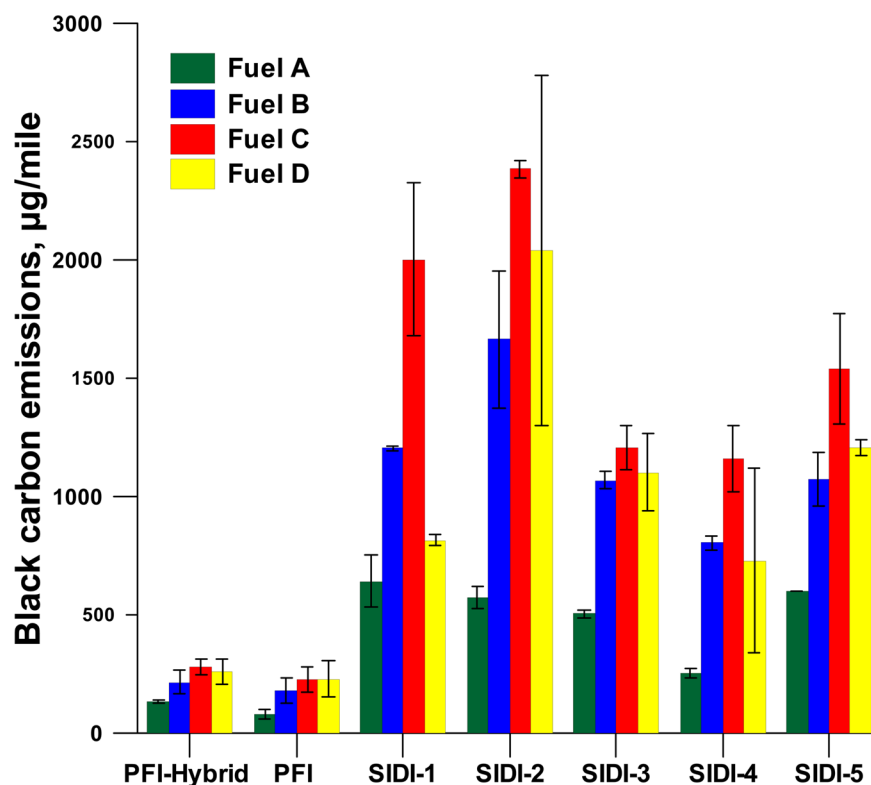


Figure 4. Black carbon emissions, expressed in $\mu\text{g}/\text{mile}$, for all vehicle/fuel combinations over the LA92 cycle. The error bars represent one standard deviation of the average values.

al.⁴⁶ Table 3 shows the total PMI for each fuel, as well as the PM indices for the main chemical groups present in gasoline. The PM mass emissions showed increases upon increasing the PMI and a good correlation with both PM mass and number emissions for all test vehicles with the exception of the PFI vehicle. Looking at the individual PM indices for each gasoline group, the PMI is an effective indicator of particulate emissions from PFI and SIDI vehicles. For example, paraffins and isoparaffins for fuel A, which were the most abundant chemical groups, showed little contribution to the total PMI compared to the total aromatics. Because the total aromatics group was the main contributor to the total PMI, subgroups of monoaromatics, naphthalenes, naphtheno/olefin-benzenes, and indenes were broken down and further analyzed. As previously discussed, higher fractions of components with higher boiling points, such as heavier normal paraffins, indenes,

mononaphthenes, and isoolefins, produced a higher PMI for fuel C compared to that of fuel D. Although there was some effects of normal paraffins on particulate emissions when comparing fuels C and D, there were clearly other factors that influenced particulate emissions when comparing fuel C to fuels A and B. The PMI for monoaromatics for fuel C was noticeably higher compared to that for fuels A and B, indicating that monoaromatic compounds were the primary hydrocarbons affecting particulate emissions. This observation is supported by the fact that the PM indices of monoaromatic compounds by carbon number group showed that C_9 aromatics accounted for $\sim 50\%$ of the monoaromatic PMI for fuel C compared to 30% and 40% for fuels A and B, respectively (see Table S7, SI). Further analysis on the PM indices by carbon number group (see Table S8, SI) showed that groups C_2-C_6 made up $\sim 45\%$ of the total mass for all fuels but only contributed 2–4% of the

total PMI. The contribution for the C₇–C₁₂ groups ranged from 96 to 98% of the total PMI, whereas they accounted for ~55% of the total mass. The C₈ group, the most abundant hydrocarbon group for fuels A, B, and D, contributed 28, 21, and 24%, respectively, of the total mass for fuels A, B, and D, but only accounted for average PM indices of 15, 12, and 17%, respectively. Conversely, the C₉ group was composed of 10, 15, 20, and 17% of the total mass for fuels A–D, respectively, yet contributed average PM indices of 24, 32, 42, and 41%, respectively.

Black carbon (BC) emissions increased with increasing aromatic hydrocarbons in gasoline, as shown in Figure 4. Similar to PM mass and number emissions, BC emissions for the SIDI vehicles were found at substantially higher levels compared to those of the PFI vehicles. The cold-start influence was also particularly noticeable in BC emissions for all test vehicles with the hot-running and hot-start phases showing relatively lower BC emissions. Previous studies have also shown higher BC emissions with SIDI vehicles compared to their PFI counterparts and a dominant cold-start effect.^{42,51,52} For the PFI vehicles, the increases in BC emissions during cold-start could be related to the incomplete vaporization of the fuel due to overfueling effects, whereas for the SIDI vehicles, the increases in BC emissions could be due to imperfect fuel mixing and fuel impingement effects.⁵² For the Tier 2 Bin2 and SULEV vehicles, the increases in BC were 126% for fuel B compared to fuel A, 34% for fuel C compared to fuel B, and 203% for fuel C compared to fuel A. Fuel C also had BC emissions that were 35% higher than those for the higher octane fuel D. It should be noted that these trends were more pronounced for the SIDI vehicles than for the PFI vehicles. For the SIDI-5 vehicle, the increases in BC were 78% for fuel B compared to fuel A, 43% for fuel C compared to fuel B, 154% for fuel C compared to fuel A, and 27% for fuel C compared to fuel D with the difference between fuels C and D being only marginally statistically significant. The drop in BC emissions for fuel D compared to fuel C could be ascribed to the lower concentrations of higher molecular weight compounds, including aromatic species and mononaphthenes in fuel D versus fuel C. It is worth noting that BC emissions correlated well with the PMI for most vehicles with R² ranging from 0.85 to 0.99 except for the SIDI-1 vehicle (R² = 0.46).

Implications. This study revealed that the use of gasoline fuels with varying aromatic contents on a fleet of seven PFI and SIDI vehicles could lead to important emission changes, especially for particulate and BC emissions. For most vehicles, the use of higher aromatic fuels led to higher CO, NMHC, and CO₂ emissions. Consistent with other studies in the literature, BTEX emissions increased with increasing total fuel aromatics content. The increases in BTEX emissions with high aromatic fuels could also have important environmental implications, because light aromatic hydrocarbons are responsible for the formation of some of the urban SOA. PM mass, number, and BC emissions increased with increasing aromatics content in gasoline, whereas direct injection fueling increased particulate and BC emissions compared to PFI fueling. This is an important finding given the predictions for SIDI vehicle penetration in the US market. In addition, BC emissions, which have been indirectly regulated for diesel vehicles in the US and Europe, will impact urban air quality and climate with the anticipation of more SIDI vehicles on the road. The results reported here also show that a higher octane number fuel with a 35% aromatic content provided emission benefits for most

vehicles, including lower THC, NMHC, CO₂, PM mass, and BTEX emissions compared to the 35% aromatic content in fuel C. The effects of altering octane by changing the composition of aromatics or the aromatics fraction were not investigated in this study. This study demonstrated that fuel aromatics play a role in the formation of particulate, BC, and gaseous toxic emissions from modern technology vehicles. Therefore, there is a need to understand the health effects of PM from vehicles when operated on fuels with varying aromatic levels.

■ ASSOCIATED CONTENT

📄 Supporting Information

Further details on fuel properties, technical information on the test vehicles, the preconditioning protocol, the emissions analyses, and the statistical analysis are provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/es5061726.

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Notes

The authors declare no competing financial interest.

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