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# Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles

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ABSTRACT

The study investigated the impact of ethanol blends on criteria emissions (THC, NMHC, CO, $NO_x$), greenhouse gas ($CO_2$), and a suite of unregulated pollutants in a fleet of gasoline-powered light-duty vehicles. The vehicles ranged in model year from 1984 to 2007 and included one Flexible Fuel Vehicle (FFV). Emission and fuel consumption measurements were performed in duplicate or triplicate over the Federal Test Procedure (FTP) driving cycle using a chassis dynamometer for four fuels in each of seven vehicles. The test fuels included a CARB phase 2 certification fuel with 11% MTBE content, a CARB phase 3 certification fuel with a 5.7% ethanol content, and E10, E20, E50, and E85 fuels. In most cases, THC and NMHC emissions were lower with the ethanol blends, while the use of E85 resulted in increases of THC and NMHC for the FFV. CO emissions were lower with ethanol blends for all vehicles and significantly decreased for earlier model vehicles. Results for $NO_x$ emissions were mixed, with some older vehicles showing increases with increasing ethanol level, while other vehicles showed either no impact or a slight, but not statistically significant, decrease. $CO_2$ emissions did not show any significant trends. Fuel economy showed decreasing trends with increasing ethanol content in later model vehicles. There was also a consistent trend of increasing acetaldehyde emissions with increasing ethanol level, but other carbonyls did not show strong trends. The use of E85 resulted in significantly higher formaldehyde and acetaldehyde emissions than the specification fuels or other ethanol blends. BTEX and 1,3-butadiene emissions were lower with ethanol blends compared to the CARB 2 fuel, and were almost undetectable from the E85 fuel. The largest contribution to total carbonyls and other toxics was during the cold-start phase of FTP.



## 1. Introduction

Currently, a key issue in the transportation sector is expanding the use of alternative and renewable fuels. Interest in alternative fuels has grown as they continue to play an important role not only in meeting the growing global demand for transportation energy but also in reducing greenhouse gas emissions [1]. To help promote the development and expansion of alternative transportation fuels, a number of government initiatives have been implemented at the regional, national, and local levels [2]. Alternative transport fuels such as hydrogen, natural gas, Fischer–Tropsch fuels, and biofuels have also been supported by regulatory organizations and environmental agencies as a viable option to reduce the transport sector contribution to local air pollution [3].

Ethanol is the most widely used renewable fuel for transportation in the United States (US) and is also used extensively in other parts of world [4,5]. As groundwater and drinking water-related issues precluded the use of methyl *tert*-butyl ether (MTBE) as an oxygenate in gasoline in the US, a transition was made to ethanol to meet nearly all oxygenate requirements [6]. With the push to use increasingly higher levels of renewable fuels, there has been an accompanying push to further increase the ethanol level in gasoline. In fact, ethanol is anticipated to comprise a predominant fraction of the volume needed to meet the US Renewable Fuel Standard (RFS), with ethanol production coming from a combination of conventional starch-based processes and more advanced technologies using cellulosic feedstocks [7].

As the composition of gasoline and other fuels continues to change, it is important to fully understand the impacts of the new fuels on exhaust emissions. While a number of studies have examined the impact of ethanol on exhaust emissions, these studies have mostly focused on ethanol levels of 10% or less [6,8–11], with a few recent studies extending to E20 [12–14]. The limited number of studies focusing on higher ethanol levels may be due to the so-called "blend wall", as 10% ethanol was previously considered the maximum level that could be used in conventional

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vehicles. Although the ethanol limit was recently raised to 15% for 2007 and newer vehicles, with prospects for increasing the limit to 15% for 2001–2006 vehicles before the end of 2010, there is not sufficient data to support the use of ethanol levels higher than 10% in older vehicles.

Studies of gasolines with ethanol contents of 10% or less have generally shown that emissions of carbon monoxide (CO), unburned hydrocarbons (HC), and non-methane hydrocarbons (NMHC) are reduced with increasing ethanol content [8,10–13,15–17]. A small increase in $NO_x$ emissions is sometimes found with additional ethanol content, but this result is not consistent among studies [6,8,10–13,18–20]. Toxic emissions are also an important consideration. Carbonyls are products from incomplete combustion from the automobile exhaust and certain carbonyls are considered to be toxic or even potential carcinogens [21]. Carbonyls in urban areas are known as key compounds of photochemically generated air pollution, since they are precursors to free radicals ($HO_x$) and PAN [22]. Other toxic species, such as benzene and 1,3-butadiene, are of particular interest in air pollution research due to their suspected role in the formation of ozone and photochemical oxidants associated with urban smog [23]. Studies have also reported some increases in carbonyl compound emissions with ethanol compared to gasoline fuel [8,20,24,25], and decreases in benzene with increasing ethanol levels [8,10,11,20,26,27]. Yet, in some studies, lower benzene emissions were also associated with lower fuel benzene levels [10,11]. Durbin et al. [6], however, found a trend of increasing benzene emissions with increasing ethanol levels for fuels with similar benzene levels and different volatility levels, indicating a potentially more complex relationship between ethanol and toxics.

The objective of the current research project was to characterize the impacts of ethanol on exhaust emissions with an emphasis on older vehicles, where such information is limited. Criteria and unregulated emissions were measured in a fleet of 7 light-duty gasoline vehicles with model years ranging from 1984 to 2007, representing Tech 3 (1981–1985), Tech 4 (1986–1995), and Tech 5 (1996–2010) technologies. Criteria emissions were $NO_x$, CO, HC, NMHC, and $CO_2$. Detailed hydrocarbon speciation was conducted for Tech 5 category vehicles only, and included carbonyl compounds (aldehydes and ketones), 1,3-butadiene, and benzene, toluene, ethylbenzene, and xylenes emissions (BTEX). Emissions and fuel consumption measurements were conducted over the Federal Test Procedure (FTP) driving cycle using a chassis dynamometer.

## 2. Experimental

### 2.1. Test fuels and vehicles

A total of six fuels were employed in the study. The fuel test matrix included a CARB phase 2 certification fuel with 11% MTBE (CARB 2) and a CARB phase 3 certification fuel with 5.7% ethanol (CARB 3). CARB 2 served as the base fuel for comparisons, as it is the fuel currently used for certification. CARB 3, with 5.7% ethanol, was used as the base fuel for creating blends with ethanol at proportions of 10 (E10), 20 (E20), 50 (E50), and 85% (E85) by volume. The main physicochemical characteristics of the test fuels are listed in Table 1.

The test matrix included seven vehicles, selected from three categories, based on their technology. Two vehicles (1984 Toyota pickup and 1985 Nissan 720 pickup) were from the Tech 3 category (1981–1985), having early three-way catalysts (TWC) with closed loop fuel control. Two vehicles (1991 Ford Explorer and 1993 Ford Festiva) were from the Tech 4 category (1986–1995), while three vehicles (1996 Honda Accord, 2000 Toyota Camry, and 2007 Chevy Silverado) were from the Tech 5 (1996–2010) category. In the Tech 5 category, one of the vehicles (2007 Chevy Silverado) was a Flexible Fuel Vehicle (FFV), which can be operated on fuels containing 85% ethanol by volume. The vehicles were chosen so that they were representative of the vehicle fleet in the State of California. The Tech 3 and Tech 4 vehicles were tested on a four fuel test matrix including the CARB Phase 2 certification fuel, the CARB Phase 3 certification fuel, E10 and E20. The FFV was tested on a six fuel test matrix including E50 and E85 ethanol blends in addition to CARB 2, CARB 3, E10, and E20. The test vehicles were all in-use vehicles recruited from private owners with an incentive.

### 2.2. Driving cycles and measurement protocol

Each vehicle was tested on each fuel over duplicate or triplicate Federal Test Procedure (FTP) cycles. The FTP is the primary emission certification cycle for light-duty vehicles in the United States (US) [28]. The FTP cycle consists of three segments or bags representing a cold start phase, a stabilized transient phase, and a hot start phase. The results of these three bags are generally weighted into a single value using a formula provided in the Code of Federal Regulations (CFR).

Prior to testing any particular vehicle, an extensive preconditioning procedure was followed: first, the oil was changed; second, the fuel was changed using a multiple drain and fill procedure with on-road conditioning to minimize carryover effects between different test fuels; third, the vehicle was run through a certification procedure portion of the preconditioning, during which it was drained of fuel and filled again to the 40% level, and then operated over the LA-4 portion of the FTP on the dynamometer; finally, the vehicle was placed into cold soak overnight prior to performing the full FTP test.

After two FTPs were completed, the data were evaluated to determine whether additional testing was required. A third test was performed only if the difference between the two composite FTP emissions test results exceeded the following: HC 33%, $NO_x$ 29%, CO 70% (provided the absolute difference in the measurements was greater than 5 mg/mi).

All tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL), which is equipped with a Burke E. Porter 48-inch single-roll electric dynamometer. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system was used to obtain certification-quality emissions measurements.

### 2.3. Emission analysis

Regulated bag and second-by-second post-catalyst emissions measurements for $NO_x$, CO, HC, NMHC, and $CO_2$ were made with a Pierburg AMA-4000 bench. Emissions of carbonyl compounds, 1,3-butadiene, and BTEX were performed in accordance with protocols developed as part of the Auto/Oil Air Quality Improvement Research Program [29], with enhancements. Samples for BTEX and 1,3-butadiene were collected using Carbotrap adsorption tubes consisting of multi-beds including a molecular sieve, activated charcoal, and carbotrap resin. For BTEX and 1,3-butadiene, the GC sample injection, column, and operating conditions were set up according to the specifications of SAE 930142HP Method-2 for $C_4$–$C_{12}$ hydrocarbons. An HP 5890 Series II GC with a flame ionization detector (FID) maintained at 300 °C was used to measure BTEX and 1,3 butadiene. A 2 m × 0.32 mm deactivated fused silica pre-column and a 60 m × 0.32 mm HP-1 column were used. The GC/FID was set up with a dual column and dual detector to allow simultaneous analysis of two GC bag samples. With the thermal desorption tubes, detection limits were improved by several orders of magnitude compared to levels achieved in earlier Auto/Oil programs.

Samples for carbonyl analysis were collected through a heated line onto 2,4-dinitrophenylhydrazine (DNPH) coated silica

**Table 1**
Main physicochemical characteristics of the test fuels.

| Property | CARB 2 | CARB 3 | E10 | E20 | E50 | E85 | Test method |
|---|---|---|---|---|---|---|---|
| Sulfur content (μg/kg) | 30.9 | 20.7 | 16.6 | 15.9 | <10 | <10 | ASTM D 2622 |
| API Gravity, 15 °C | 60.1 | 59.1 | 58.3 | 56.8 | 51 | 44.2 | ASTM D 287 |
| Net heating value (MJ/kg) | 42.58 | 42.27 | 41.21 | 39.79 | 33.34 | 26.74 | ASTM D 240 |
| Distillation | | | | | | | ASTM D 86 |
| IBP | 336 | 100.5 | 319.5 | 330.7 | 328.3 | | |
| 50 | 518.9 | 520 | 520.5 | 520.6 | 521 | | |
| 90 | 608.6 | 611.3 | 546.4 | 546.3 | 547.5 | | |
| 95 | 635.1 | 639 | 552.6 | 553.3 | 554.4 | | |
| FBP | 661.7 | 662.4 | 569.6 | 564.7 | 569.1 | | |
| Research Octane Number (RON) | 97.4 | 96.2 | 98.4 | 101 | 101.2 | 101.7 | ASTM D 2699 |
| Motor Octane Number (MON) | 88.8 | 87.8 | 88.8 | 89.8 | 91.7 | 92.5 | ASTM D 2700 |
| Reid vapor pressure (psi) | 6.65 | 6.67 | 7.2 | 6.92 | 6.57 | 5.49 | ASTM D 5191 |
| Benzene (wt.%) | 1.1 | 0.86 | 0.76 | 0.73 | 0.43 | 0.09 | ASTM D 5580 |
| Toluene (wt.%) | 6.45 | 11.28 | 9.97 | 8.56 | 5.46 | 1.21 | |
| Ethylbenzene (wt.%) | 5.46 | 1.54 | 1.36 | 1.78 | 0.85 | <0.1 | |
| *p/m* Xylenes (wt.%) | 5.55 | 5.12 | 4.53 | 4.27 | 2.56 | 0.74 | |
| *o*-Xylene (wt.%) | 0.58 | 1.03 | 0.91 | 0.78 | 0.51 | <0.1 | |
| ⩾C9 Aromatics (wt.%) | 9.62 | 12.08 | 10.66 | 9.53 | 5.87 | 1.22 | |
| Total aromatics, (wt.%) | 28.76 | 31.9 | 28.2 | 25.65 | 15.67 | 3.25 | |
| Ethanol (wt.%) | <0.1 | 6.63 | 11.33 | 17.19 | 43.54 | 74.95 | ASTM D 5599 |
| MTBE (wt.%) | 11.54 | <0.1 | <0.1 | 1.48 | 0.18 | <0.1 | |
| Total oxygen (wt.%) | 2.09 | 2.3 | 4.16 | 6.86 | 17.12 | 29.56 | |
| Olefins (mass%) | 5.5 | 5 | 4.8 | 4.2 | 2.8 | 0.5 | ASTM D 6550 |

*Note*: ASTM method D5599 is specified for use on blends of ethanol up to 20%, so the lower than expected values for the E50 and E85 blends can probably be attributed to issues in measuring ethanol with that method at those levels.

cartridges (Waters Corp., Milford, MA). Sampled cartridges were extracted using 5 mL of acetonitrile and injected into an Agilent 1100 series high performance liquid chromatograph (HPLC) equipped with a diode array detector. A 5 μm Deltabond AK resolution (200 cm × 4.6 mm ID) with upstream guard column was used and the HPLC sample injection and operating conditions were set up according to the specifications of the SAE 930142HP protocol.

## 3. Results and discussion

### 3.1. Criteria emissions and fuel consumption

Weighted average $NO_x$ emissions of the FTP cycle are shown in Fig. 1. Results show that fuel impact on $NO_x$ emissions varied by vehicle. Three vehicles (1984 Toyota pickup truck, 1985 Nissan pickup, and 1993 Ford Festiva) showed increasing $NO_x$ emissions as ethanol content increased. The trend was statistically significant for two (1984 Toyota and 1993 Ford Festiva) of the three vehicles. Increases in $NO_x$ for the 1984 Toyota were 4.9, 14, and 19.5% for CARB 3, E10, and E20, respectively, compared with CARB 2. For the 1993 Ford Festiva, $NO_x$ increases relative to CARB 2 were 13.2 for E10 and 24.6% for E20. The newer vehicles (1996 Honda Accord, 2000 Toyota Camry, 2007 Chevrolet Silverado) did not show statistically significant trends in $NO_x$ emissions, although ethanol blends generally had lower emissions than CARB 2.

Increasing $NO_x$ emissions with increasing ethanol content in the older vehicles may be due to differences in catalyst technology, aging, or effectiveness. Previous studies with larger vehicle fleets have shown trends of increasing $NO_x$ emissions with increasing ethanol content [6,8,10,12], though other studies have shown no changes, inconsistent changes, or even decreases in $NO_x$ emissions [11,13,30]. Higher fuel oxygen content in the fuel can lean out the air–fuel mixture, which, in turn, can lead to higher $NO_x$ emissions. Older technology vehicles do not have as sophisticated controls of air–fuel ratios at the levels of oxygen investigated in this study, so

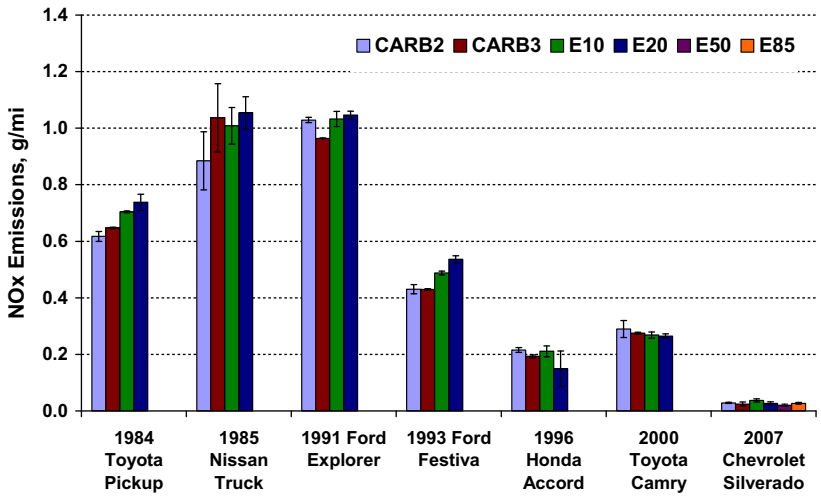


**Fig. 1.** Average $NO_x$ emissions for all fuel/vehicle combinations over FTP operation.

can be more impacted by increases in ethanol/oxygen in the fuel. A study by NREL showed that vehicles that did not apply long-term fuel trim during wide open throttle operation ran leaner under these conditions as the oxygen content in the fuel increased [13].

Trends in emissions from newer vehicles indicate a more complex set of factors may be at work. For newer vehicles, Durbin et al. [6] found some increases in $NO_x$ with increasing ethanol content, but these trends showed a dependence on fuel volatility. As the fuels in the current study were splash blended, fuel parameters, such as volatility, would have also been varied in conjunction with ethanol content. Thus, for different vehicles, the effects of different fuel properties may have an interaction with the ethanol effects. In recent work with newer vehicles, a consistent increase in $NO_x$ emissions with increasing ethanol content was seen in a study that used a full design approach for fuel properties to compensate for potentially interacting fuel variables [12], while no consistent trends for $NO_x$ were seen in a study where the ethanol content was adjusted by splash blending [13]. Ethanol also has a higher latent heat of vaporization, which can lower flame temperature in the combustion process, thereby contributing to lower $NO_x$ emissions [31].

THC and NMHC emissions over the FTP test cycle are presented in Fig. 2a and b. Total THC/NMHC emissions are an order of magnitude lower for newer vehicles as compared to older vehicles for all fuels tested, as would be expected with the more advanced emission control technologies seen in new vehicles. Four vehicles (1984 Toyota pickup, 1985 Nissan pickup, 1993 Ford Festiva, and 1996 Honda Accord) showed decreasing trends in THC and NMHC emissions as the ethanol content of the fuel increased. Among these four vehicles, the observed trend was statistically significant for the two oldest vehicles (1984 Toyota and 1985 Nissan). Reductions (relative to CARB 2) of −17.4 and −22.7% for E10 and E20, respectively, were seen in the 1984 Toyota pickup. Reductions of −12.2 for CARB 3, −8.1 for E10, and −23% for E20 were seen in the 1985 Nissan pickup. Other vehicles did not show emissions differences for THC and NMHC with varying ethanol levels, with the exception of the 2007 Chevy Silverado, which showed increases in THC and NMHC emissions when the E85 fuel was used.

Trends of decreasing THC/NMHC emissions with increasing ethanol content have generally been seen in studies utilizing larger fleets of older vehicles [8,10–13]. For Tier 1 and newer vehicles, a wider range of results have been seen, with many studies showing decreases in THC/NMHC with increasing ethanol content [12,13,30], and some studies showing no change, or even an increase in THC/NMHC emissions, with increasing ethanol content [6,32]. Reductions in THC emissions may be attributed primarily to the presence of oxygen in the fuel, which leans the air–fuel ratio and promotes oxidation during combustion and over the catalyst. The higher octane number for ethanol blends can also promote more efficient combustion [33]. The more mixed results for Tier 1 vehicles indicate that more complex factors may be at play for THC/NMHC emissions in newer vehicles. Modern vehicles generally tend to have better control of the air–fuel ratio and can adjust the air–fuel ratio to compensate for different levels of ethanol in

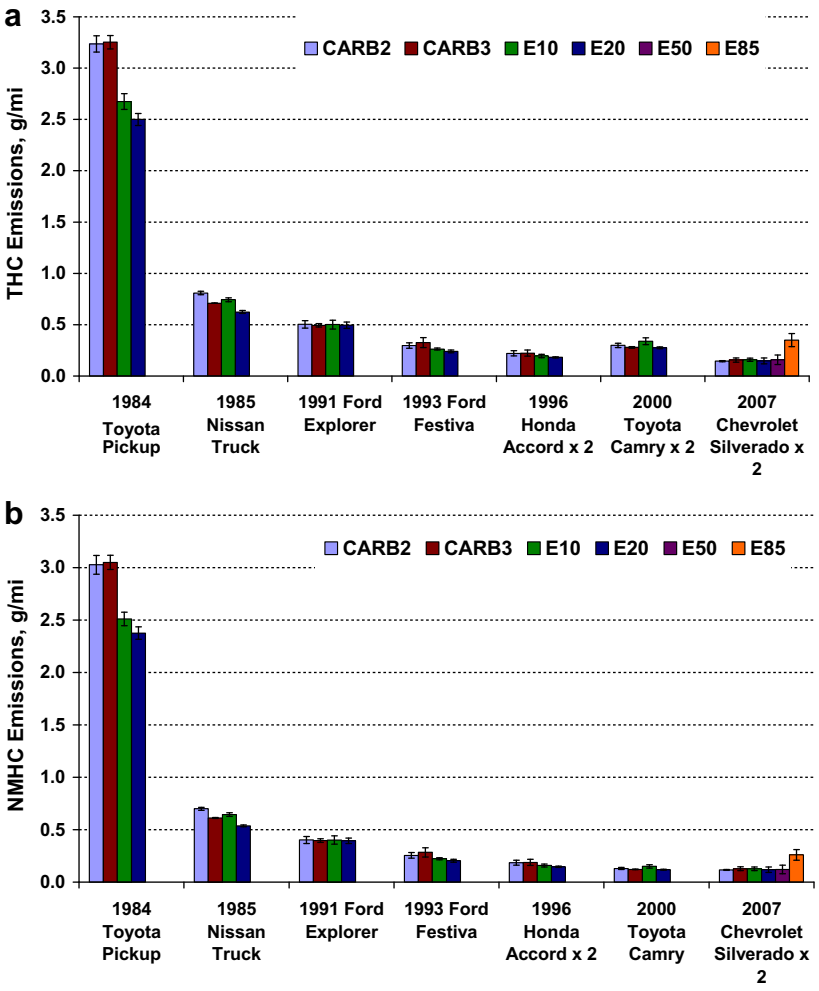


**Fig. 2.** (a and b) Average emissions of THC (a) and NMHC (b) for the test fuels over FTP.

the fuel, although the ability make these adjustments differs between vehicles under conditions such as wide open throttle (WOT) [13,34]. Durbin et al. [6] also showed that the interaction with fuel volatility may be an important factor. The observed increase in THC/NMHC emissions from the FFV when operated using E85 was mainly due to the lower volatility of the fuel blend, which makes the fuel more difficult to vaporize under cold-start conditions. Increases in THC/NMHC emissions were also observed during the cold-start phase of the FTP (bag 1), where they were on the order of 20–40 times higher than for the bags 2 and 3 for the E85 fuel in the FFV. In general, cold-start THC emissions (bag 1) ranged from 0.267 to 0.740 g/mi, whereas bag 2 and bag 3 emissions ranged from 0.012 to 0.020 g/mi and 0.023 to 0.038 g/mi, respectively. For the E85 fuel, bag 1 emissions were 0.740 g/mi, while bag 2 and bag 3 emissions were 0.020 and 0.038 g/mi, respectively.

Fig. 3 shows CO emissions for all vehicle/fuel combinations. CO emissions displayed an inverse relationship of decreasing emissions with increasing ethanol level for the 1984 Toyota pickup, 1985 Nissan pickup, 1991 Ford Explorer, and 1996 Honda Accord. The relationship was statistically significant for the two oldest vehicles and the 1996 Honda Accord. The largest, statistically significant reductions in CO emissions were for E20 (relative to CARB 2; −72.2% for the 1984 Toyota, −36.4% for the 1985 Nissan, and −32.8% for the 1996 Honda Accord). While the two later model vehicles did not demonstrate a significant impact on CO emissions, a decreasing trend in emissions with higher ethanol levels was observed. The general trend of decreasing CO emissions with increasing ethanol content is consistent with previous studies [6,8,10–13,32], and reductions may be ascribed to the fuel-borne oxygen, which leans the air–fuel ratio and improves oxidation during combustion and over the catalyst [18,35].

Fig. 4a and b shows $CO_2$ emission and fuel economy results, respectively, for the test vehicles over the FTP. $CO_2$ emissions did not show any significant trends between the fuels. Fuel economy decreased with increasing levels of ethanol for the five later model vehicles, as shown in Fig. 4b. Fuel economy changes were statistically significant for the 2000 Toyota Camry and 2007 Chevrolet Silverado, but not for the other vehicles. The largest reductions in fuel economy were seen in the 2007 Chevy Silverado with the E50 and E85 ethanol blends, which were −16.2 and −29%, respectively, relative to CARB 2. Reductions in fuel economy with increasing ethanol content can be attributed to the lower energy content of the oxygenated ethanol, as shown in Table 1.

### 3.2. Unregulated emissions

Carbonyl emissions (aldehydes and ketones) were obtained from two of the seven vehicles. A total of thirteen carbonyls were identified and quantified in the exhaust. Fig. 5a and b shows the carbonyl compounds emitted from the 1996 Honda Accord (a) and the 2007 FFV Chevrolet Silverado (b). Consistent with previous findings [20,21,36,37], formaldehyde, acetaldehyde, and acetone were the most prominent carbonyl compounds for both vehicles. High molecular weight carbonyl compounds were also present, but in significantly lower amounts. For the 1996 Honda Accord, emission levels of acrolein, propionaldehyde, valeraldehyde, tolualdehyde, and hexanaldehyde were below the detection limits of the method for all test fuels. For the FFV, in addition to the above compounds, crotonaldehyde, MEK, and methacrolein were almost undetectable. However, only tolualdehyde was found in detective levels for the E85 fuel.

For toxic emissions, acetaldehyde showed the most consistent trend, increasing with ethanol content for both vehicles. For the 1996 Honda Accord, acetaldehyde emissions increased for the E10 blend by 71% and 98%, while E20 increased 202% and 251%, compared with CARB 2 and CARB 3. For the 2007 Chevy Silverado, significant increases in acetaldehyde were only seen with the use of the E85 fuel, with increases on the order of 1097% (compared to CARB 2) and 1430% (compared with CARB3). Acetaldehyde emissions for E10 were −39% and −23% lower than CARB 2 and CARB 3. The changes in acetaldehyde emissions for E20 and E50 were within the experimental variability. Previous studies have generally shown consistent increases in acetaldehyde emissions with increasing ethanol content [6,8,10,11,13,17,32], as ethanol is the main precursor of acetaldehyde in vehicular emissions.

For the 2007 Chevrolet Silverado, the blends of E10, E20, and E50 resulted in reductions in formaldehyde emissions, when compared to CARB 2. The reductions were −44% for E10, −36% for E20, and −27% for E50. Compared to CARB 3, only E10 resulted in limited reductions (−5%) of formaldehyde emissions, while E20 and E50 increased emissions by 8–23%, respectively. The use of E85 resulted in significant increases in formaldehyde emissions – an 88% increase when compared to CARB 2 and a 216% increase when compared with CARB 3. The increased formaldehyde emissions for E85 may be attributed to the presence of ethanol, and the higher oxygen content in the fuel, as well as decreases in fuel aromatics, because these compounds do not participate in formaldehyde formation [38]. For the 1996 Honda Accord, the use of CARB 3 resulted in a 14% decrease in formaldehyde emissions, when compared with

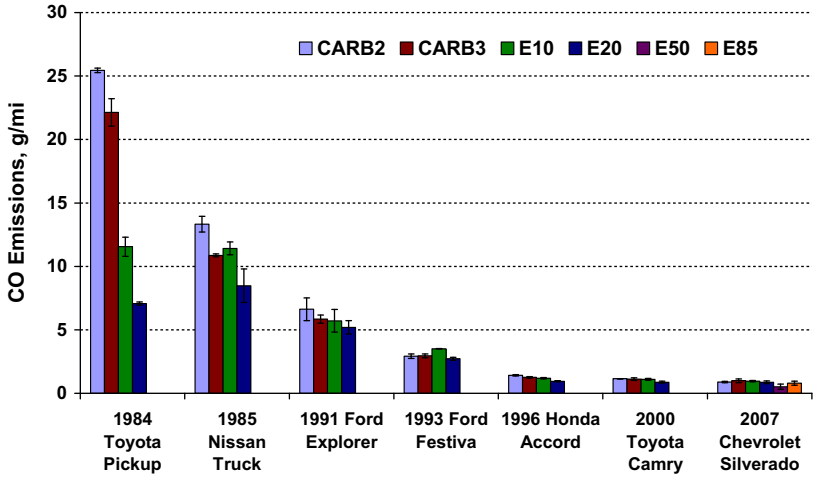


**Fig. 3.** CO emissions for all fuel/vehicle combinations over FTP operation.

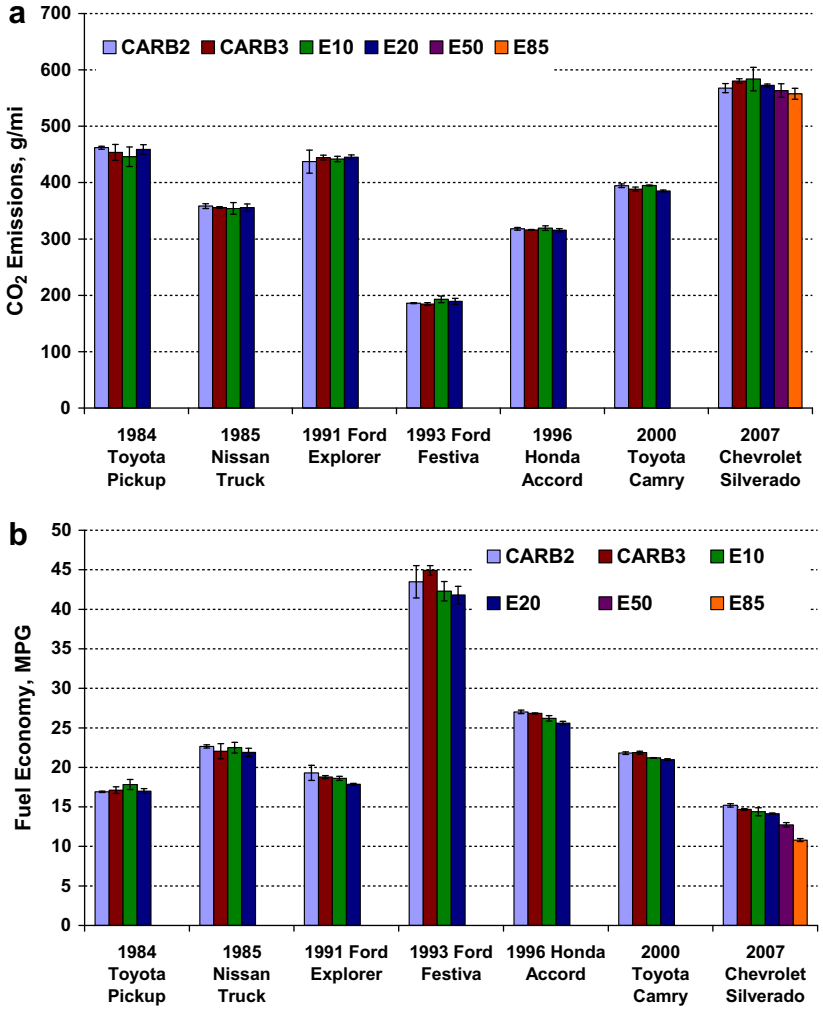


**Fig. 4.** (a and b) $CO_2$ emission results (a) and fuel economy (b) for all fuel/vehicle combinations over FTP operation.

CARB 2, with E10 following closely behind showing a 10% reduction, though the reductions were not statistically significant. E20 showed no changes in formaldehyde emissions, which is consistent with previous studies that have shown no or inconsistent changes in formaldehyde emissions as a function of ethanol content [6,8,10,11].

Acetone emission reductions were seen in both the 1996 Honda and the 2007 Chevy Silverado. The 1996 Honda showed reductions in acetone emissions of 39–56%, with higher ethanol levels related to the greater reductions. For the 2007 Chevrolet Silverado, the highest acetone reductions were achieved with E10, with reductions of 63% (compared to CARB 2) and 60% (compared to CARB 3). Higher molecular weight carbonyls were found at fairly low levels for the 1996 Honda Accord and none of the emission changes were statistically significant. Ethanol blended fuels all had higher crotonaldehyde emissions than CARB 2 for the 1996 Honda, as well. In fact, the use of CARB 3, E10, and E20 resulted in increases in crotonaldehyde emissions of 486%, 510%, and 327%, when compared to CARB 2.

Fig. 6 shows the influence of cold-start conditions on total carbonyl emissions for all fuel/vehicle combinations. Total carbonyl emissions were higher for the 1996 Honda Accord when run on E10 and E20; the 2007 Chevy Silverado had higher emissions on the CARB 3 fuel and also had high emissions when run on E85. The impact of the cold-start on emissions was particularly noticeable for both vehicles. Total carbonyl emissions were found at substantially higher levels during the first phase of the driving cycle, when the engine was cold and the catalyst was below its light-off temperature. On the other hand, exhaust concentrations of most carbonyl compounds were quite low, or below the detection limit during the second and the third phases of the FTP. Increased exhaust temperature and higher performance of the catalytic converter after light-off were the main reasons for the decrease in carbonyls during the second and third phases of the FTP.

The 2007 Chevy Silverado also showed significant increases in total carbonyl emissions when run on E85, compared to the CARB specification fuels and other ethanol blends. Compared to CARB 2, total carbonyl emissions for the E85 blend increased by 1240% during the cold-start FTP and by 138% for the weighted FTP. Compared to CARB 3, total carbonyl emissions for E85 increased by 329% for cold-start FTP and 109% for the weighted FTP. As shown in Fig. 5b, the increase in carbonyl emissions was largely due to increases in acetaldehyde emissions. The increases could be due to the lower volatility of the E85 blend, as compared to the blends with higher gasoline levels, which makes it especially difficult to vaporize, or the vehicle engine control module (ECM) may not be adjusting properly to the higher ethanol content, resulting in higher hydrocarbon emissions.

Fig. 7a and b shows the BTEX and 1,3-butadiene emissions over the FTP for the 1996 Honda Accord (a) and 2007 Chevrolet Silverado (b). It should be noted that ethylbenzene was almost undetectable for all fuels and both vehicles. For the 1996 Honda Accord,

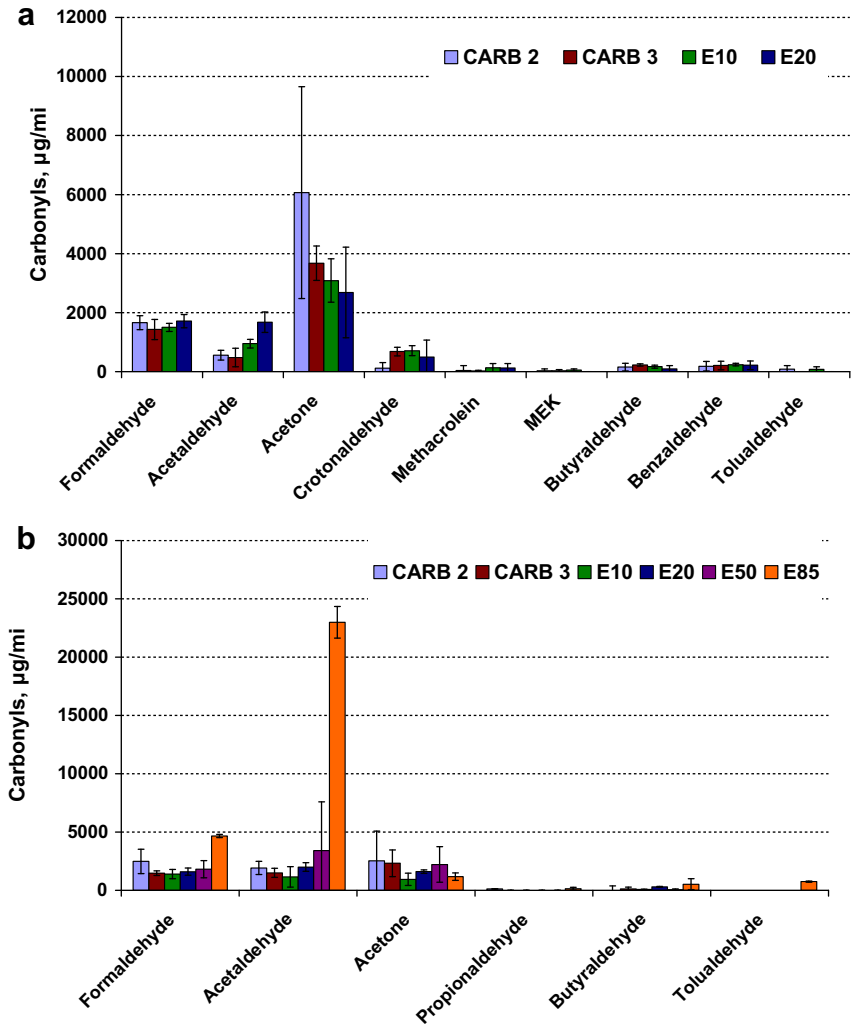


**Fig. 5.** (a and b) Individual carbonyl compound emissions for the 96 Honda Accord (a) and the 07 FFV Chevrolet Silverado (b) over FTP operation.

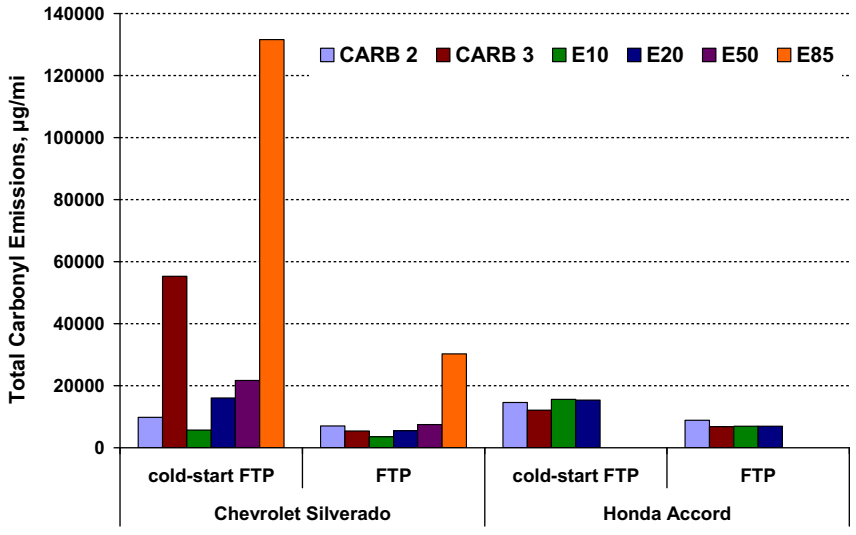


**Fig. 6.** Total carbonyl emissions for both vehicles over the cold-start FTP (phase 1) and FTP driving cycles.

BTEX and 1,3-butadiene emissions were significantly higher for CARB 2 than the other fuels. As with previous studies, which have shown that benzene decreases with increasing ethanol levels, the current study showed that E20 had lower benzene, as well as

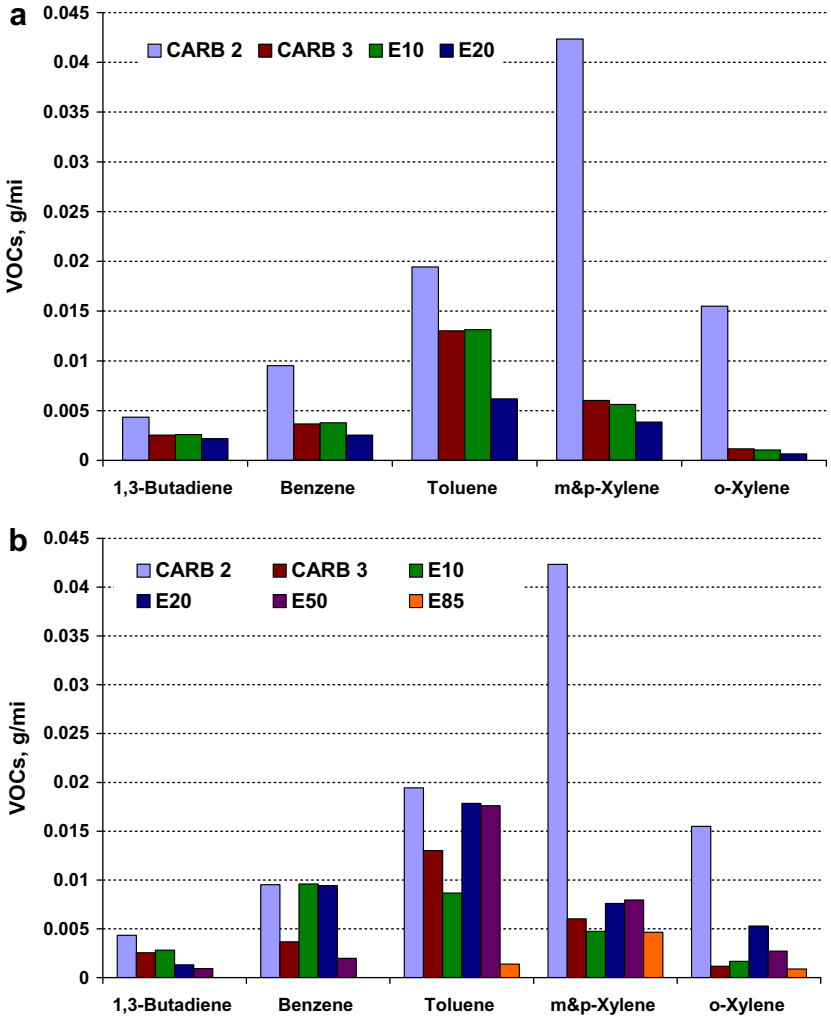


**Fig. 7.** (a and b) 1,3-Butadiene and BTEX emissions for the 96 Honda Accord (a) and the FFV Chevrolet Silverado (b) over FTP operation.

toluene and xylene emissions than either CARB 3 or E10 [8]. Benzene levels for the 2007 Chevrolet Silverado did not show a consistent trend – benzene levels were undetectable for E85 and were lower for CARB 3 and E50 (compared to CARB 2), while benzene levels for E10 and E20 were similar to those of CARB 2. Table 1 shows that the lower emissions of BTEX species for the E20 blend may be due to lower levels of total aromatics in the fuel. The benzene emissions also follow a trend that is roughly consistent with the benzene level in the fuel. Benzene is formed from either unburned fuel-borne benzene or benzene formed during combustion of other aromatic and non-aromatic compounds found in gasoline [39]. Previous studies have shown that benzene generally decreases with increasing levels of ethanol, with this trend primarily be attributable to benzene levels in the fuel [8]. The higher BTEX emissions for CARB 2 do not appear to be directly attributable to fuel aromatic levels or oxygen content. Although the CARB 2 fuel did have the highest levels of benzene, ethylbenzene, and *m/p* xylenes, the CARB 3 and E10 fuels had either higher or comparable levels of toluene, *o*-xylene, and total aromatics.

Similar conclusions about fuel aromatic levels cannot be drawn about 1,3-butadiene (which is characterized as a human carcinogen and as precursor for secondary formation of formaldehyde and acrolein), because it is a product of fuel fragmentation and is not present originally in the fuel [40,41]. Previous studies have not shown consistent trends for 1,3-butadiene, either [6,8,11,17]. Yet, in the current study, the 2007 FFV Chevrolet Silverado, showed a consistent decreasing trend in 1,3-butadiene, with emissions decreasing as ethanol level increased. Emissions of 1,3-butadiene were undetectable for E85 and E50 showed a reduction of 78% compared to CARB 2. Benzene levels for the 2007 Chevrolet Silverado did not show consistent trends with increasing ethanol levels. Benzene levels were undetectable for E85 and were lower for CARB 3 and E50 compared to CARB 2, while benzene levels for E10 and E20 were similar to those for CARB 2. The latter phenomenon may be due to the fact that the addition of oxygenated compounds such as ethanol inhibits the oxidation of benzene. It is therefore possible that an increase in soot volume fraction may result in some increases for benzene emissions [42].

For other BTEX compounds, toluene, and *m*-, *p*-, and *o*-xylene, the highest emissions were found for CARB 2, while E20 and E50 showed higher emissions of these species than the other ethanol blends, i.e., CARB 3, E10, and E85. The substantially lower BTEX emissions for E85 relative to the other blends is presumably due to the higher oxygen content and the lower amount of aromatic compounds in the fuel, although the other fuels did not generally follow this trend. For both the 1996 Honda and the 2007 Chevy, emissions of BTEX and 1,3-butadiene were mostly produced during the cold-start of FTP, while their concentration levels during the second and third hot-start phases were negligible.

## 4. Conclusions

The study of regulated and unregulated emissions profiles of gasoline-powered light-duty vehicles included models ranging in years from 1984 to 2007. The vehicles covered three categories (Tech 3, Tech 4, Tech 5) and represented different engine and exhaust aftertreatment technologies; one Flexible Fuel Vehicle (FFV) was included. Test fuels included a CARB phase 2 certification fuel with an 11% MTBE content, a CARB phase 3 certification fuel with a 5.7% ethanol content, E10, E20, E50, and E85. Regulated and unregulated emission and fuel consumption measurements were performed over the FTP using a chassis dynamometer in at least duplicate for each vehicle/fuel test combination.

The THC and NMHC emission increased for E85, but not the lower ethanol blends for the 2007 FFV Chevrolet Silverado. The CO emissions showed similar trends to those of THC and NMHC emissions, with earlier model vehicles showing a statistically significant decrease as the ethanol level increased. Ethanol did not have a significant impact on CO for the newer vehicles, however. The experimental results showed mixed trends for $NO_x$, with some older vehicles showing an increase in $NO_x$ emissions as ethanol level increased. The newer vehicles did not show any statistically significant impacts of ethanol on $NO_x$ emissions, although the ethanol blends generally had lower emissions than the CARB 2. $CO_2$ emissions did not show any significant trends between the fuels. In addition, fuel economy showed a decrease with increasing levels of ethanol for the five latest model vehicles. This is consistent with the lower energy content for the fuels with higher ethanol contents.

In general, carbonyl emissions were lower for the ethanol blends than those of CARB 2 and CARB 3 fuels, with the exception of the E85 fuel. The predominant compounds were formaldehyde, acetaldehyde and acetone, while heavier carbonyls were only detected in very low concentrations for all fuels and both vehicles. Carbonyl emission levels were higher for the 1996 Honda Accord than those of the 2007 FFV Chevrolet Silverado. The most consistent trend for carbonyl emissions was an increase in acetaldehyde emissions with increasing ethanol, which is consistent with ethanol being a precursor for the formation of acetaldehyde. It should be mentioned that the use of E85 resulted in significantly higher formaldehyde and acetaldehyde emissions than for the CARB fuels and the other ethanol blends. The largest contribution to total carbonyl emissions was during the cold-start phase of the FTP, when the engine was cold and the catalyst was below its light-off temperature.

Similar to carbonyl emissions, 1,3-butadiene and BTEX emissions were found in lower levels for the 2007 Chevrolet Silverado than the 1996 Honda Accord. In general, the addition of ethanol resulted in lower toxic emissions for the Honda Accord, compared to the CARB 2 fuel, with E20 having the lowest BTEX emissions. For the Chevrolet Silverado, 1,3-butadiene showed the most consistent trends, with CARB 2 having the highest emissions and emissions decreasing as a function of ethanol level. For toluene, and *m-, p-*, and *o*-xylene, for the 2007 Chevrolet Silverado, the highest emissions were found for the CARB 2 fuel, while the E20 and E50 fuels interestingly showed higher emissions of these species than the other ethanol blends, i.e., CARB 3, E10, and E85. Benzene and 1,3-butadiene emissions were undetectable and other aromatics were at low levels for the E85 fuel.

The results show some consistent trends with increasing ethanol content for some vehicles, but for other vehicles it appears that a more complex set of factors are impacting the emissions results. The older vehicles showed the most consistent trends for the regulated emissions, with reductions in THC/MNHC and CO emissions and increasing $NO_x$ emissions with increasing ethanol content. This can be attributed to the leaning of the air–fuel mixture with the increasing levels of ethanol/oxygen in the fuel, and the inability of the ECM to adjust to this change. For the vehicles that did not show consistent trends for the regulated emissions, these vehicles may be less sensitive to changes in fuel properties or may have ECMs that can readily adjust to the ethanol content in the fuel, or some other factors may be in play, such as interactions with other correlated fuel properties like fuel volatility, or combustion-related effects like changes in the adiabatic flame temperature. The unregulated emissions showed some trends with decreasing BTEX emissions with increasing ethanol for the 1996 Honda Accord and very low levels of toxic aromatics for the E85 fuel for the 2007 Chevrolet Silverado, but the BTEX emissions did not appear to be directly correlated to fuel aromatic levels, although the CARB 2 fuel did have the highest levels of benzene, ethylbenzene, and *p/m* xylenes. Overall, the results indicate that the impact of ethanol on emissions for the in-use gasoline vehicle fleet can depend on a number of factors, including the mix of vehicle technologies and the ability of these vehicles to adjust to the level of ethanol in the fuel, the sensitivities of different vehicles to changes in ethanol content, interactions with other fuel properties, such as volatility, as well as other potential factors.

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