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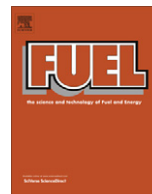Karavalakis, Georgios
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# Impact of olefin content on criteria and toxic emissions from modern gasoline vehicles

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## HIGHLIGHTS

▶ Changing the olefin content had a minor impact on exhaust emissions.
▶ Fuel olefin content had no statistically significant effect on $NO_x$, THC, NMHC, and CO emissions.
▶ Some fuel effects were observed for fuel economy and $CO_2$ emissions.
▶ 1,3-Butadiene emissions increased with increasing fuel olefin content.
▶ Benzene, formaldehyde, and acetaldehyde did not show statistically significant fuel effects.

## ARTICLE INFO

## ABSTRACT

Olefins are an important component of gasoline and an important property with respect to the development of reformulated gasolines using regulatory models. Currently, the coefficients used in regulatory gasoline development models are primarily based on studies conducted in the early 1990s, as an extensive study of olefin gasoline effects has not been conducted since that time. The goal of this study was to evaluate the impact of gasoline fuel olefin content on modern vehicles compliant with US EPA Tier 2 standards. Vehicles were tested with two fuels with different olefin contents, nominally 3% and 15% by volume, over the LA92 test cycle. The results showed that changing the olefin content with the range in this study had a relatively minor impact on exhaust emissions of these latest technology vehicles, including total hydrocarbons (THCs), nitrogen oxides ($NO_x$), and carbon monoxide (CO) emissions as well as toxic emissions such as formaldehyde, acetaldehyde, and benzene. Only exhaust 1,3-butadiene emissions showed significantly higher emissions at higher olefin levels, consistent with a correlation between olefins in the fuel and in the exhaust. This information from this study will be used to provide updates of fuel properties effects for use in the EPA Complex Model and the CARB Predictive Model.

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## 1. Introduction

In an effort to improve ambient air quality in urban areas, the United States (US) and other countries throughout the world have implemented a number of regulations over the past several decades [1,2]. The US Environmental Protection Agency (EPA), as a part of its efforts to implement the Clean Air Act, has mandated the use of reformulated gasoline in nonattainment regions in the United States [3]. Federal and California regulations utilize models or sets of equations (i.e., the Complex Model (EPA) and the Predictive Model (California Air Resources Board-CARB) that describe the im-

pact of fuel properties and composition on emissions and are used to develop and evaluate these reformulated gasolines [4,5]. These models are used by refiners to determine if the gasoline they are producing meets the emissions performance standards under the EPA's reformulated gasoline (RFG) program [5–7]. A number of studies were conducted in the early 1990s, including the Auto/Oil Air Quality Improvement Research Program (AQIRP) and studies by the EPA, to provide the initial basis for these models [8–13]. The Energy Policy Act of 2005 requires that EPA update the Complex Model to reflect the latest information on fuel and vehicle effects. This has provided the emphasis for a number of collaborative programs between the EPA, the Department of Energy (DOE), and the Coordinating Research Council (CRC) in recent years [14,15].

One of the major components of gasoline are olefins (alkenes), along with a mixture of other hydrocarbons, including paraffins (alkanes), naphthenes (cycloalkanes), and aromatics, and oxygenates [16]. Olefins are hydrocarbon compounds with one or more carbon double bonds. Olefins can increase the reactivity of gasoline fuels in combustion processes [17], and also improve fuel octane number and anti-knock performance [16,18,19]. However, high olefin content fuels have some disadvantages, such as higher olefin content exhaust emissions that have a higher ozone formation potential (OFP) [17], and also an increased tendency to form deposits in engine injectors and intake valves [16]. Reducing the olefin content of a fuel and substituting with paraffins reduces the reactivity of the fuel, which can lead to a less complete combustion. It has also been shown that reducing olefin content decreases the emissions of 1,3-butadiene, which is photo-reactive and contributes to photochemical smog [18].

Olefin content was one of the main fuel parameters evaluated in the AQIRP and EPA studies in the early 1990s [8–11,13,17]. These earlier studies showed that the impacts of olefins on the combustion process lead to measureable differences in exhaust emissions for vehicles of this earlier generation [8–11,13,17]. In the AQIRP program, reducing olefins from 20% to 5% was found to increase hydrocarbons emissions by 5.8 ± 2.0% and reduce $NO_x$ emissions by 6.1 ± 1.9% in a fleet of 1989 vehicles, and to increase hydrocarbon emissions by 5.7 ± 3.0% and reduce $NO_x$ by 6.7 ± 1.9% in a fleet of 1983–1985 vehicles [8]. EPA studies of this time showed similar trends of lower $NO_x$ emissions with lower olefin content, but they did not see any impact of olefins on hydrocarbon emissions [11]. Studies of the impact of olefin content on modern vehicles exhaust emissions are fewer and less comprehensive, and have generally shown less consistent trends [17,20–23]. Additionally, while recent studies, such as those by CRC and EPA, have more extensively evaluated the emissions impacts of fuel properties such as sulfur content, $T_{50}$, $T_{90}$, ethanol content, aromatics content, and Reid Vapor Pressure (RVP) in modern vehicles [14,15,17], the impact of olefin content on exhaust emissions has not been extensively studied since the early 1990s.

The goal of this study is to provide a more comprehensive evaluation of the effect of olefin content on the exhaust emissions from the latest technology gasoline vehicles. In this study, the impact of olefin content on regulated and toxic exhaust emissions was evaluated for fifteen 2008 model year vehicles compliant with Tier 2 emissions standard regulations. Vehicles were tested with two fuels with different olefin contents, nominally 3% and 15% by volume, while being operated over the LA92 test cycle. Statistical analyses were then conducted to determine the significance of any observed fuel trends. This study is part of the larger series of studies by CRC, EPA, and DOE to evaluate fuel property impacts in modern vehicles [14,15]. This information will be used to provide updates of fuel properties effects for use in the EPA Complex Model and the CARB Predictive Model [24].

## 2. Experimental

### 2.1. Test fuels

Two gasoline fuels, denoted A and B, with different olefin content (nominally 3% and 15% in volume) were tested. The olefins levels were chosen so as to span the 10th and 90th percentile of US fuels based on survey data at the time the study was being planned. Except for olefin content, other fuel properties were designed to be equivalent within the specified ranges. Table 1 summarizes the selected fuel properties. These fuels were specially blended from standard refinery gasoline blending streams with a detergent additive, but without using any special chemicals or chemical blendstocks. Prior to testing, the engine oil was changed and the vehicles were conditioned for 2000 miles on a mileage accumulation dynamometer using the Standard Road Cycle.

### 2.2. Test vehicles

Fifteen 2008 Tier 2 USA EPA vehicles, eight passenger cars and seven light-duty trucks, were tested. The characteristics of the vehicles are provided in Table 2. All of these vehicles had been used in a recently completed, congressionally-mandated study jointly sponsored by EPA, DOE and CRC to measure the effects of changes in selected fuel properties on light-duty vehicle exhaust emissions [25]. All vehicles were equipped with three way catalyst (TWC) and exhaust gas recirculation (EGR) technology with heated oxygen ($HO_2$) sensor.

### 2.3. Driving cycle and test matrix

A test matrix with fully randomized order of test fuels for every test vehicle was used. The randomization of fuels A and B for every vehicle could be sequenced as AABB, ABBA, ABAB, or variations on these sequences. The randomization sequence for each vehicle is provided in Table S-1 in the Supporting information. The test cycle used in this program was the LA92 (also known as Unified) Cycle which is shown in Fig. S-1 in the Supporting information.

At least two replicates were performed on every vehicle/fuel combination. After the completion of two LA92 tests on each vehicle/fuel combination, the data was evaluated to determine if additional testing is required. A third test was performed if differences in LA92 regulated emissions exceeded a predefined limit using the criteria that were developed by Painter and Rutherford [26] and have been used in previous studies [27,28]. A third test was performed if the difference in the measurements exceeded the following: THC 33%, $NO_x$ 29%, CO 70%. Since the emissions levels of modern vehicles are considerably lower than those for vehicles at the time these criteria were developed, this criteria was only applied if the absolute difference in the measurements was greater than 5 mg/mi. Based on these limits, triplicate tests were required on 13 of the 30 vehicle combinations. This is more than the number of replicates required in previous similar studies [27,28], which could be attributed to the more aggressive nature of the LA92 cycle compared to the Federal Testing Procedure (FTP). The emissions measurements for the third test included both regulated and toxic emissions.

### 2.4. Fuel conditioning

Before testing a vehicle/fuel combination, the vehicle was preconditioned on a new fuel with a procedure that included a fuel drain and fill (40%), followed by a catalyst sulfur purge cycle and four coast downs (70–30 mph). For the catalyst sulfur purge cycle, the inlet catalyst temperature and the exhaust A/F ratio were monitored with an OBDPRO serial scantool that was connected to the engine control unit (ECU). Either one or two additional drain and fills were done on each vehicle. The need for two additional drain and fills for some vehicles was based on the information obtained in the E-89/V2/EPACT program [25]. The vehicles requiring an extra drain and fill are identified in Table 2. The vehicle was then preconditioned over a single iteration of bags 1 and 2 of the LA-92 cycle on the dynamometer before the actual emissions test was conducted. An additional 15 min drive at 50 mph was conducted when the first fuel was tested on each vehicle to help condition the vehicle for the program. This sequence is shown schematically in Fig. S-2 in the Supporting information.

Following the initial emissions test, the vehicle was either placed into cold soak if the next test is on the same fuel or it under-

**Table 1**
Selected fuel properties.

| Property | Test method | Units | Limits | Fuel A | Fuel B |
|---|---|---|---|---|---|
| Olefins | ASTM D1319 | Vol.% | | 3.1 | 14.76 |
| API gravity | ASTM D4052 | API | Report | 58.58 | 57.8 |
| DVPE | ASTM D 5191 | psi | 7.5–7.8 | 7.61 | 7.54 |
| $T_{10}$ | ASTM D 86 | °F | Varies w/RVP | 132.6 | 134.2 |
| $T_{50}$ | ASTM D 86 | °F | 195–205 | 200.7 | 204.1 |
| $T_{90}$ | ASTM D 86 | °F | 310–320 | 312.6 | 316.9 |
| FBP | ASTM D 86 | °F | <437 | 365.5 | 363.9 |
| RON | ASTM D 2699 | | 91–95 | 94.6 | 94.6 |
| MON | ASTM D 2700 | | 83–87 | 85.9 | 84.5 |
| (R + M)/2 | | | 87–91 | 90.1 | 89.6 |
| Benzene | ASTM D 5580/3606 | Vol.% | 0.9–1.1 wt.% | 1.01 | 1.05 |
| Aromatics | ASTM D 1319 | Vol.% | 23–27 | 23.0 | 25.25 |
| Sulfur | ASTM D 5453 | ppm | 25–30 | 27.1 | 25.3 |
| Ethanol | ASTM D 4815 | Vol.% | 10 | 9.83 | 10.02 |
| Carbon | | wt.% | | 84.13 | 84.01 |
| Hydrogen | | wt.% | | 13.07 | 12.37 |
| H/C ratio | | | | 0.155 | 0.147 |
| Gross heating value | ASTM D4809 | BTU/lb | | 19,160 | 19,091 |
| Carbon content per unit of energy | | lbs. Carbon/BTU | | $4.39 \times 10^{-5}$ | $4.40 \times 10^{-5}$ |

**Table 2**
Tested vehicles.

| No. | Year | Make | Model | Engine family | PC | LDT | Engine | Primary mileage | Extra drain and fill | Standard |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2008 | Dodge | Caliber | 8CRXB02.4ME0 | X | | 2.4L I4 | 9811 | | Tier 2 Bin 5 LDV/LDT |
| 2 | 2008 | Ford | F-150 | 8FMXT05.44HF | | X | 5.4L V8 | 10,528 | | Tier 2 Bin 8 LDT4 |
| 3 | 2008 | Ford | Explorer | 8FMXT04.03DB | | X | 4.0L V6 | 12,204 | | Tier 2 Bin 4 LDT3, CA-LEVII ULEV |
| 4 | 2008 | Ford | Focus | 8FMXV02.0VD4 | X | | 2.0L I4 | 9979 | | Tier 2 Bin 4 LDV, CA-LEVII ULEV |
| 5 | 2008 | GM | Silverado | 8GMXT05.3373 | | X | 5.3L V8 | | | Tier 2 Bin 5 |
| 6 | 2008 | GM | Impala | 8GMXV03.9052 | X | | 3.5L V6 | 10,226 | | Tier 2 Bin 5, CA-LEVII LEV |
| 7 | 2008 | GM | Cobalt | 8GMXV02.4025 | X | | 2.2L I4 | | | Tier 2 Bin 5, CA-LEVII LEV |
| 8 | 2008 | GM | Outlook | 8GMXT03.6151 | | X | 3.6L V6 | 10,341 | | Tier 2 Bin 5, CA-LEVII LEV |
| 9 | 2008 | Honda | Odyssey | 8HNXT03.54KR | | X | 3.5L V6 | 10,166 | X | Tier 2 Bin 5 LDT3, CA-LEVII ULEV LDT2 |
| 10 | 2008 | Honda | Civic | 8HNXV01.8LKR | X | | 1.8L I4 | 11,051 | X | Tier 2 Bin 5, CA-LEVII ULEV |
| 11 | 2008 | Jeep | Liberty | 8CRXT03.7NE0 | | X | 3.7L V6 | | | Tier 2 Bin 5 |
| 12 | 2008 | Nissan | Altima | 8NSXV02.5G5A | X | | 2.5L I4 | | X | Tier 2 Bin 5, CA-LEVII LEV |
| 13 | 2008 | Toyota | Camry | 8TYXV02.4BEA | X | | 2.4L I4 | 9917 | X | Tier 2 Bin 5, CA-LEVII ULEV |
| 14 | 2008 | Toyota | Corolla | 8TYXV01.8BEA | X | | 1.8L I4 | 10,445 | X | Tier 2 Bin 5, CA-LEVII ULEV |
| 15 | 2008 | Toyota | Sienna | 8TYXT03.5BE4 | | X | 3.5L V6 | 10,501 | X | Tier 2 Bin 5, CA-LEV-II ULEV LDT |

PC: passenger car; LDT: light-duty truck.

**Table 3**
Percentage differences of different emissions comparing fuel B with fuel A.

| | $NO_x$ | THC | NMHC | CO | $CO_2$ | 1,3-Butadiene | Benzene | Formaldehyde | Acetaldehyde | Fuel economy |
|---|---|---|---|---|---|---|---|---|---|---|
| Bag 1 | **18.3%** | NS | NS | **−14.8%** | <u>1.0%</u> | NS | NS | NS | NS | NS |
| Bag 2 | <u>−20.7%</u> | NS | NS | NS | **0.9%** | NS | NS | NS | <u>−59.5%</u> | <u>−0.9%</u> |
| Bag 3 | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| Weighted | NS | NS | NS | NS | **0.9%** | **26.4%** | NS | NS | NS | <u>−0.8%</u> |

*Notes*: Bold values are statistically significant $p \leqslant 0.05$; underlined values are marginally statistically significant $0.05 < p \leqslant 0.1$; positive values represent increases for fuel B relative to fuel A, whereas negative values represent decreases for fuel B relative to fuel A; NS: no statistically significant percentage differences.

went the full procedure for new fuels, as discussed above and shown in Fig. S-2 in the Supporting information. In cases where back-to-back tests were conducted on the same vehicle/fuel combination and the period between these tests exceeded 36 h, for example, over the weekend, an additional phase 1 and phase 2 LA92 cycle was conducted on that vehicle prior to testing.

### 2.5. Emissions measurements

Vehicle emissions measurements were conducted in Vehicle Emissions Research Laboratory (VERL) at the University of California, Riverside, Center for Environmental Research and Technology (CE-CERT). The VERL is equipped with a 48-inch Burke E. Porter single-roll electric chassis dynamometer, capable of testing vehi-

cles weighing up to 12,000 lbs. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system was used to obtain the emissions measurements.

For each LA92 test, normal bag and modal tailpipe measurements were made for THC, NMHC, $NO_x$, CO, $CO_2$ and fuel economy. The VERL configuration utilizes a Pierburg AMA-4000 emissions bench for the measurement of both normal bag emissions and second-by-second dilute post-catalyst measurements. Emissions measurements were also carried out for benzene, 1,3-butadiene, formaldehyde and acetaldehyde for every phase of each test. These measurements were performed in accordance with protocols developed previously as part of the Auto/Oil Air Quality Improvement Research Program [29–31]. Given the low levels of emissions for the individual species that are found for the more advanced

vehicles being tested, we have also incorporated some procedures to enhance the detection level. This includes the use of Carbotrap adsorption tubes and a Gerstel TDS thermal desorption unit for sample injection for 1,3-butadiene and benzene. With the use of Carbotrap absorption tubes, the amount of sample that is collected and injected into the Gas Chromatography (GC) is considerably greater than when using Tedlar bag samples, thus, the detection limits with the thermal desorption tubes are improved by several orders of magnitude compared to levels achieved in earlier Auto/ Oil programs. For this program, for example, the volume sampled and subsequently injected into the GC using the Carbotrap absorption tubes was the equivalent of 365 ml for bags 1 and 3 and 1400 ml for bag 2, in comparison with the 5 ml of sample injected with some previous studies that employed Tedlar bags [29–31].

## 2.6. Statistical analysis

Statistical analyses for each pollutant were run using the Mixed procedure in the PC/SAS application from SAS Institute, Inc. [32]. The mixed models were performed for each pollutant to determine the statistical significance of any fuels effects. The fixed effect included in the model was the fuel type and the random effect was the vehicle. The type 3 ANOVA was also performed and the analysis results are summarized in the Table S-2 to Table S-21 in the Supporting information.

The normality of residuals was checked in the models for all regulated and toxic emissions to determine if a transformation was necessary. Analyses using the logarithmic transform of the data in similar previous studies have shown that the emissions standard deviation is relatively constant as a percentage of the emission level. For example, vehicles with higher emission levels will tend to have a higher variability on an absolute basis than those with lower emission levels. Examination of the current data revealed that this relationship between the emissions level and variability held true even for the very low emitting vehicles. All the emissions except for formaldehyde and acetaldehyde were analyzed on the natural logarithm scale. The fuel economy was analyzed on the inverse scale (i.e., gallons/mile). Formaldehyde and acetaldehyde were analyzed in the arithmetic scale because the assumption of normality for the residual was not violated for these emissions, so no transformation was necessary.

ANOVA results were considered to be statistically significant for $p \leqslant 0.05$, although we also note cases where $0.05 < p \leqslant 0.1$ as marginally statistically significant in the text. Pairwise comparisons were made using a least squares means test. The results from the ln or inverse models were "back transformed" to provide least square means for all pollutants on each fuel. This provides an arithmetic measure to evaluate the magnitude of any statistically significant effects. Any constants added to facilitate the analysis in the logarithmic scale were subsequently subtracted from the least square means once the back transformation to the arithmetic scale was made. For emissions components that included zeros for individual bags or weighted emissions, a small constant was added prior to taking the logarithm to allow the analyses to be done in the logarithmic scale. Any added constants were selected to be as small as possible, and in all cases did not exceed the background levels.

## 3. Results and discussion

The weighted LA92 emissions and fuel economy results for the testing of fifteen vehicles are presented in the following figures, along with the least square means from the statistical analysis. The results for each vehicle/fuel combination represent the average of all test runs on that particular combination. The error bars rep-

resent one standard deviation on the average values for the individual vehicles and the pooled standard deviation for the least square means. Table 3 summarizes percentage differences of different emissions comparing fuel B with fuel A.

It should be noted that in some cases, results of different bags of the emissions test were essentially at the background level. As such, the initial data set included some negative values. Since it is unlikely that emissions would be eliminated as part of the combustion process, and to facilitate data analysis, negative values were replaced by zero in the final data set used for the statistical analysis and for the figures presented. For the statistical analyses, results are considered to be statistically significant for $p$ values less than 0.05. Results were considered to be marginally statistically significant where $p$ values is between 0.05 and 0.1.

### 3.1. NO$_x$ emissions

NO$_x$ emissions were below 25 mg/mi for more than half of the vehicles, as shown in Fig. 1. There were no statistically significant differences between the two fuels for the weighted and bag 3 emissions. For the cold-start (bag 1) phase of the cycle, statistical analyses indicated statistically significant NO$_x$ emissions increases (18.3%) with fuel B. While, for bag 2, a marginally statistically significant ($p = 0.07$) decrease, with fuel B showing 20.7% lower NO$_x$ than fuel A was observed.

Previous studies of older vehicles have shown stronger olefin effects on NO$_x$ emissions. These studies indicate that NO$_x$ emissions increase with olefin content [8,9,11,17,33–35]. The higher NO$_x$ emissions with more olefin in the fuel could be attributed to the more reactive nature of the olefins, which in turn can lead to more complete combustion and greater heat release during combustion [17]. However, some slightly more recent studies have shown less significant impacts for olefins on NO$_x$ emissions [20–22].

### 3.2. THC and NMHC emissions

THC and NMHC weighted emissions are shown in Fig. 2a and b. THC and NMHC emissions were generally in the range of 50 and 40 mg/mi, respectively, or less. Statistical analyses did not show any significant differences between fuels A and B for THC or NMHC for the weighted emissions or any of the individual bag emissions.

Previous studies have shown stronger olefin effects for older vehicles, with hydrocarbons emissions decreasing with increasing olefin content [8,9,17,33,34]. This could be due to the more reactive nature of the olefins compared to paraffins, which leads to a more complete combustion in the chamber and to a more complete oxidation of olefins over the catalyst [17]. Less significant impacts for olefins on hydrocarbon emissions, however, have been found in some slightly more recent studies [20–22].

### 3.3. CO emissions

CO emissions vary from vehicle to vehicle. More than half of the vehicles had CO emissions below 1 g/mi, and only three vehicles had CO emissions of 3 g/mi or more, as presented in Fig. 3. There were no statistically significant differences in CO emissions between the two fuels for the weighted and the bags 2 and 3 emissions. Fuel effect were statistically significant for the cold-start (bag 1) phase of the cycle. Fuel B CO emissions were lower than fuel A.

The lack of strong trends for CO emissions as a function of olefin content is consistent with a majority of the previous studies in the literature [8,9,17,21,33–36]. This can be attributed to the fact that olefins do not affect the stoichiometry of combustion. Therefore, they do not have a significant impact on the formation of rich combustion zones where CO is primarily produced [17].
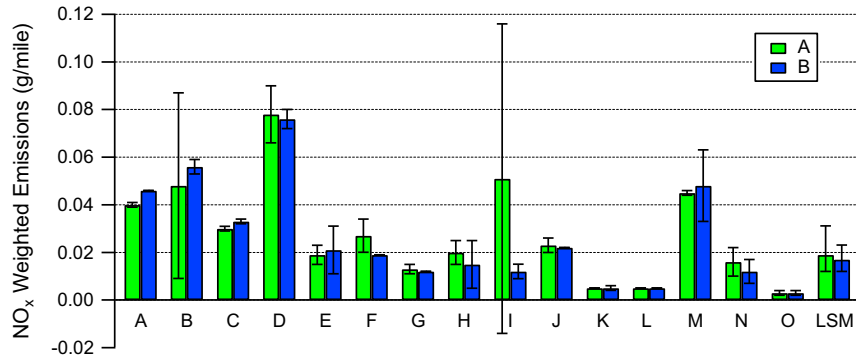
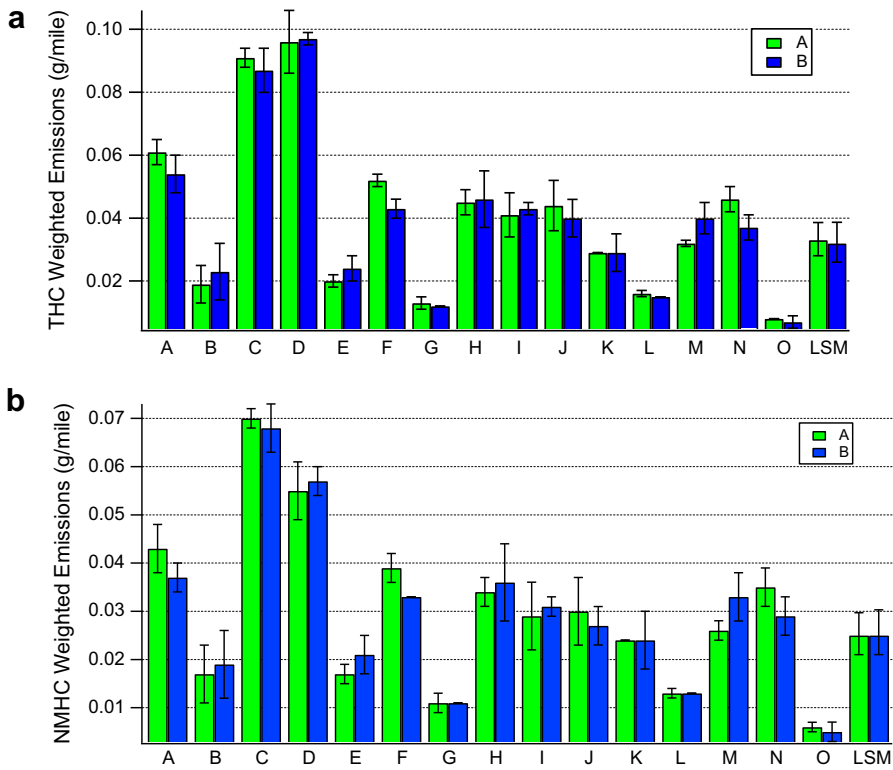**Fig. 1.** Average NO$_x$ weighted emission results.



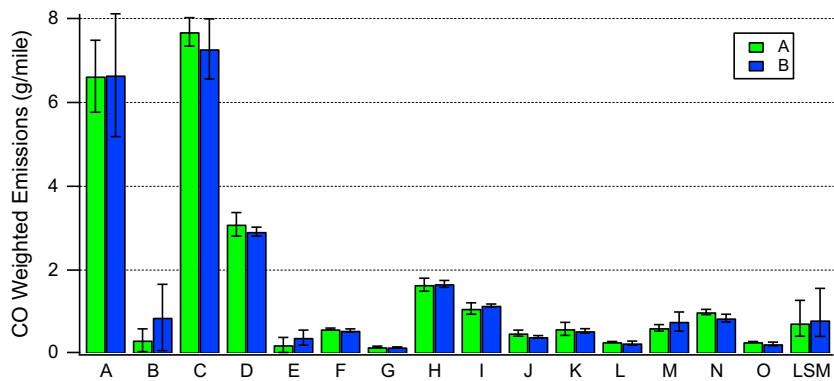**Fig. 2.** (a and b) Average THC and NMHC weighted emission result.



**Fig. 3.** Average CO weighted emission results.

## 3.4. $CO_2$ emissions and fuel economy

$CO_2$ emissions did show some slight statistically significant trends between the fuels, as shown in Fig. 4a. Statistically significant differences were found for the weighted and bag 2 $CO_2$ emissions, and a marginally statistically significant difference ($p = 0.09$) was found for bag 1 $CO_2$ emissions, with higher $CO_2$ for fuel B than fuel A for each of these cases. Bag 3 $CO_2$ emissions did not show statistically significant differences between fuels. The increases in $CO_2$ for fuel B compared to fuel A were 0.9% for weighted results, 1% for bag 1, and 0.9% for bag 2. No statistically significant differences between fuels were found for the bag 3 $CO_2$ emissions.

It is not immediately clear why $CO_2$ emissions would show differences between the two fuels. Looking at the data for the individual vehicles more closely, thirteen of the fifteen vehicles had higher weighted $CO_2$ emissions for fuel B than fuel A. $CO_2$ differences could be attributed to differences in the carbon content per unit of energy for the fuels. However, the carbon contents per unit of energy for these fuels were very similar (a difference of 0.2%), as shown in Table 1. The H/C ratio for fuel B is also slightly lower than that of fuel A, and this difference is on the order of 0.8%, which could indicate that C–C bonds provide a greater fraction of the energy for the combustion process for fuel B [37]. A few studies have focused on the impact of fuel olefin content on $CO_2$ emissions for spark ignition engines. These studies, which were performed on both older and modern vehicles, did not show any significant fuel olefin content impacts on $CO_2$ emissions, however [11,21]. Further investigation would likely be needed to better understand the nature of the $CO_2$ results.

Fuel economy results are presented in Fig. 4b. The results for individual vehicles showed trends that were consistent with the standard EPA fuel mileages for the respective vehicles. Fuel economy did show some marginally statistically significant differences between the fuels for the weighted ($p = 0.06$) and bag 2 ($p = 0.08$).

While, no statistically significant differences between fuels for the bags 1 and 3 was seen. For both the weighted and bag 2 results, the fuel economy for fuel B was 0.8–0.9% lower than that for fuel A. This is consistent with the results seen for the $CO_2$ emissions. Again, the nature of these fuel economy differences is not immediately clear, as the energy contents of the two fuels are very similar. Ferrell et al. showed higher fuel economy with increased olefin content, but this was for a direct injection engine, and is the opposite of the trend found in our work [38]. Some previous studies have also shown that octane number can impact fuel economy/engine efficiency, and the octane number for fuel A was slightly higher than for fuel B. These studies have generally been for much larger differences in the octane number or in fuel type (e.g., with and without ethanol), however, and the effects are very dependent on the driving condition and the specific vehicle [39–42].

## 3.5. Benzene, 1,3-butadiene, formaldehyde, and acetaldehyde emissions

The results for the four measured toxics are provided in Figs. 5a and b and 6a and b. The results show differences in the toxic emission rates for different vehicles, although these differences did not seem to be attributable to either certification level or vehicle type (i.e., cars vs. truck). For toxic emissions, 1,3-butadiene showed a statistically significant fuel effect ($p = 0.049$) for the weighted emissions, with 26.4% higher emissions for fuel B than fuel A (Fig. 5a). No statistically significant differences between fuels were seen for the individual bags for 1,3-butadiene, however. In comparison, previous studies of older vehicles have shown trends of 1,3-butadiene increasing with higher levels of olefins [8,9,17,35]. Several studies have also shown that 1,3-butadiene is a combustion intermediate formed from olefinic, cyclohexane, and cyclohexene precursors [43–47]. This is consistent with the observed correlations between olefins in the fuel and in the exhaust [10,44,48]. Kai-
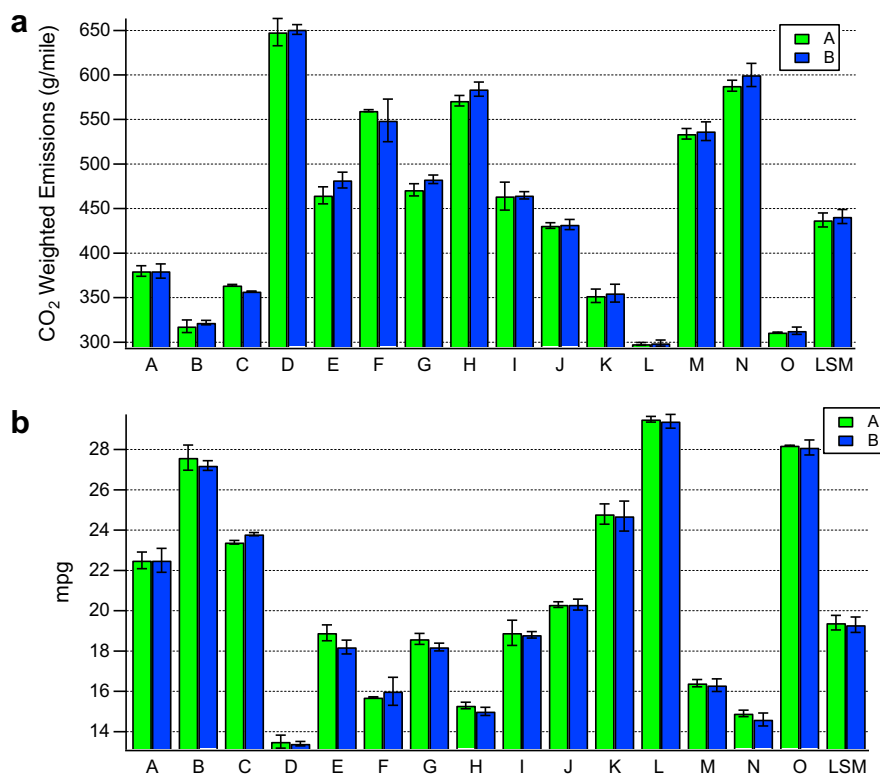


**Fig. 4.** (a and b) Average $CO_2$ weighted emission and weighted fuel economy results.
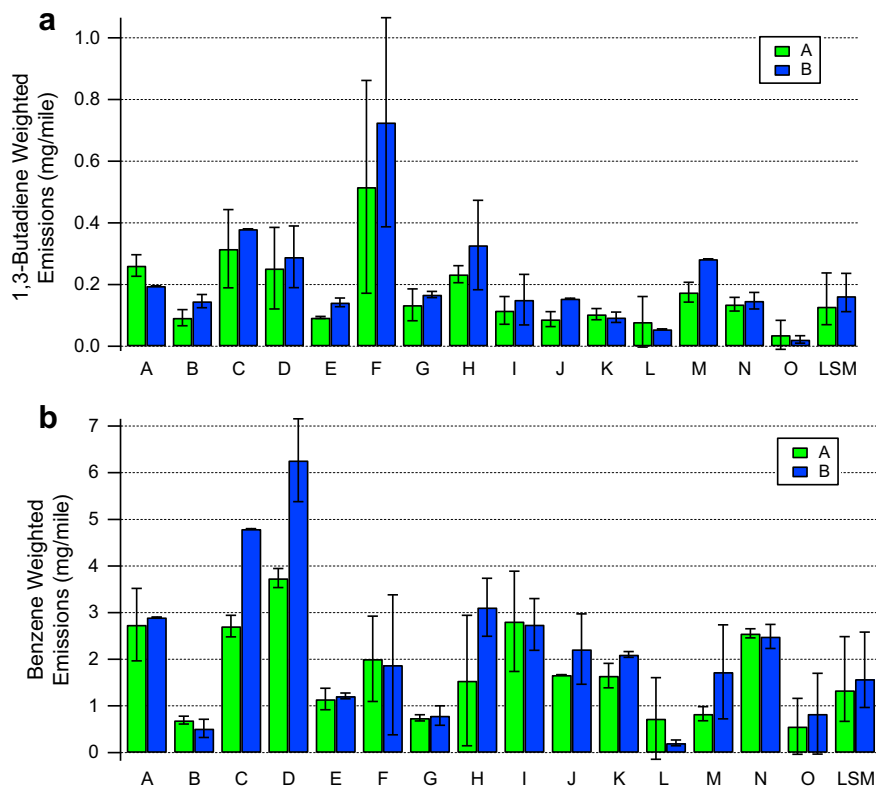
**Fig. 5.** (a and b) Average 1,3-butadiene and benzene weighted emission results.

ser et al. also observed that straight-chain alkene fuels produced significant amounts of 1,3-butadiene, whereas a branched alkene produced much less 1,3-butadiene [43,46]. It should be noted that benzene emissions did not show strong effects with olefins, as shown in Fig. 5b.

Formaldehyde and acetaldehyde emissions are shown in Fig. 6a and b). The results revealed that formaldehyde was the most abundant compound among carbonyls, followed by acetaldehyde, and these compounds are the major contributors to the total carbonyl emissions. The other aldehydes, including the high molecular weight compounds of valeraldehyde, hexanal, and crotonaldehyde, and the aromatic aldehydes of benzaldehyde, were below the detection limits of the method for both fuels. It was found that formaldehyde and acetaldehyde emissions did not show strong effects with olefins. Only bag 2 acetaldehyde emissions showed a marginally statistically significant difference ($p = 0.054$), with fuel B having 59.5% lower emissions than fuel A.

The majority of previous studies have also found that olefins do not have a significant impact on the other primary toxics, i.e., benzene, formaldehyde, and acetaldehyde [8,9,17,35]. It should be noted that some vehicle/fuel combinations showed higher variability for the different toxic species than others. A closer examination of these data points shows that in many cases this could be attributed to greater variability in the bag 1 emissions in most cases, although in some cases higher variability in bag 2 was also observed.

## 4. Conclusions

Changing the olefin content within the range of this study had a relatively minor impact on exhaust emissions of the latest model vehicles compliant with Tier 2 emissions standards. Fuel olefin content had no statistically significant effect on the weighted val-

ues and also for most of the individual bag emissions for the primary regulated pollutants ($NO_x$, THC, NMHC, and CO) and for the benzene, formaldehyde, and acetaldehyde toxics. The primary impact found for olefins was increasing emissions of 1,3-butadiene with increasing olefin levels, with the weighted emissions showed a statistically significant fuel effect for the weighted 1,3-butadiene emissions for fuel B being 26.4% higher emissions than for fuel A. This is consistent with a correlation between olefins in the fuel and in the exhaust. Statistically significant differences were observed in both the weighted and bag 2 $CO_2$ emissions, and a marginally statistically significant difference was found for bag 1 $CO_2$ emissions, with higher $CO_2$ for fuel B than fuel A for each of these cases. Some statistically significant increases in $CO_2$ and decreases in fuel economy were also seen for fuel B compared to fuel A. These differences were on the order of 0.8–1.0%, but did not appear to be related to either the energy content of the fuel or the carbon content per unit of energy in the fuel.

In a broader sense, the results of this study suggest that the impact of olefins or other fuel components on exhaust emissions will diminish as modern gasoline vehicles with advanced combustion control and aftertreatment systems become more prevalent in the in-use fleet. This is consistent with the trends seen in previous studies in the literature. Studies of older technology vehicles have shown stronger impacts for olefins in decreasing hydrocarbon emissions and increasing $NO_x$ emissions, consistent with the more reactive nature of olefins that can lead to more complete combustion. Other studies of more modern vehicles, on the other hand, have shown less consistent olefin effects. It does appear that fuel composition may have an impact on the individual hydrocarbon species in the exhaust, such as 1,3-butadiene. Further study would be needed to understand how these differences might impact ozone or overall exhaust toxicity. While this could indicate that regulations on fuel composition will have diminishing returns over time, it is important to note that this study, and most studies of
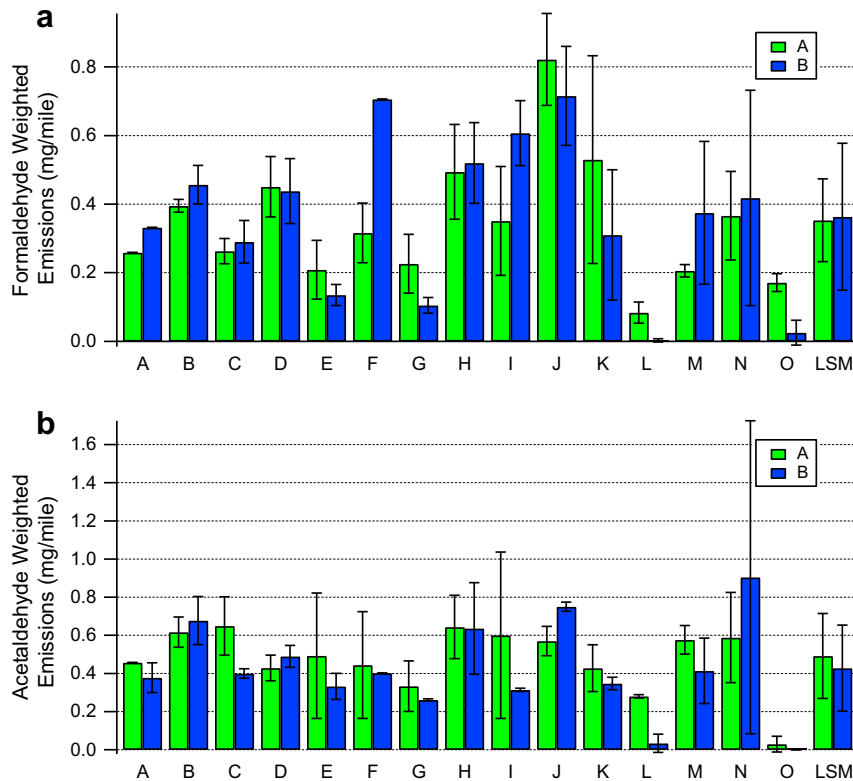
**Fig. 6.** (a and b) Average formaldehyde and acetaldehyde weighted emission results.

fuel effects to date, have focused on conventional gasoline vehicles. It is expected that gasoline direct injection (GDI) vehicles will represent an increasing fraction of the in-use fleet going into the future, in order to meet standards for improving fuel economy. Further study is needed to see if differences in fuel composition might have a stronger impact in modern GDI vehicles, as opposed to more conventional gasoline vehicles.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2012.12.031.

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