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Regulated Emissions, Air Toxics, and Particle Emissions from SI-DI Light-Duty Vehicles Operating on Different Iso-Butanol and Ethanol Blends

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ABSTRACT

Gasoline direct injection (GDI) engines have improved thermodynamic efficiency (and thus lower fuel consumption) and power output compared with port fuel injection (PFI) and their penetration is expected to rapidly grow in the near future in the U.S. market. In addition, the use of alternative fuels is expanding, with a potential increase in ethanol content beyond the current 10%. Increased emphasis has been placed on butanol due to its more favorable fuel properties, as well as new developments in production processes.

This study explores the influence of mid-level ethanol and iso-butanol blends on criteria emissions, gaseous air toxics, and particulate emissions from two wall-guided gasoline direct injection passenger cars fitted with three-way catalysts. Emission measurements were conducted over the Federal Test Procedure (FTP) driving cycle on a chassis dynamometer. This study utilized seven fuels with varying ethanol and iso-butanol contents, including E10, E15, E20, Bu16, Bu24, Bu32, and a mixture of E20 and Bu16 resulting in E10/Bu8. Emissions included nitrogen oxides (NO_x), carbon monoxide (CO), total hydrocarbons (THC), non-methane hydrocarbons (NMHC), methane (CH_4), and carbon dioxide (CO_2). Additionally, carbonyl compounds, 1,3-butadiene, benzene, ethylbenzene, toluene, and xylenes were quantified in the exhaust. Total particle number emissions, black carbon, and real-time particle size distributions were also measured. The results are discussed in the context of the changing fuel type and composition.

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INTRODUCTION

Spark ignition (SI) engines are anticipated to be the dominant form of propulsion in the passenger car market segment for the predictable future. Improving the overall efficiency of gasoline powered passenger cars, directly connected to meeting stringent carbon dioxide (CO_2) emission limits, is the main focus of today's engine combustion development work. To reach CO_2 targets, different strategies have been studied, including engine downsizing and higher boost pressures in combination with direct gasoline injection. Direct Injection SI engines can offer up to 25% improvement in fuel economy compared with port-fuel injected (PFI) SI engines [1]. This is mainly achieved through reductions in pumping and heat losses when operated unthrottled at low-mid loads. DI fueling for gasoline engines significantly improves engine power, which allows the engine displacement volume to be reduced for a given application, even while the engine performance improves. In addition, gasoline DI engines reduce the tendency of a fuel to knock because of enhanced charge cooling, allowing the compression ratio to be increased for higher efficiency [2, 3, 4].

The penetration of gasoline DI vehicles in the U.S. market is rapidly increasing. It is foreseen that this category of vehicles will dominate the gasoline market, eventually replacing conventional and less efficient PFI vehicles. It is interesting to note that in the U.S., half of all light-duty vehicle certifications for the 2012 model year included gasoline DI engines, reaching approximately 24% of the market, up from virtually 0% in 2007. This trend is expected to dramatically increase, with a projection of 48% and 93%, respectively, of all new vehicles having gasoline DI by 2016 and 2025 [5].

One of the drawbacks of gasoline DI engines is the increase in particulate emissions in comparison to PFI engines, due to combustion in fuel rich regions in the cylinder [6]. Aakko and Nylund [7] found that particle mass emissions for a gasoline DI vehicle were an order of magnitude higher than for a PFI vehicle for the European 70/220/EEC drive cycle. Similar findings were reported by Liang et al. [8] when they tested two Euro 4 type vehicles fitted with a DI and a PFI fueling, respectively, over the NEDC. Analogous to particle mass (PM) emissions, particle number emissions have also been reported to be higher with SIDI vehicles in comparison to their PFI counterparts. Ristimaki et al. [9] showed significantly higher solid and semi-volatile particle number emissions when they tested two Euro 3 PFI and DI gasoline vehicles over the European ECE15 and EUDC cycles. Szybist et al. [10] reported that particle number emissions with DI fueling were increased by 1-2 orders of magnitude compared to PFI fueling.

In addition to the new engine technologies, there is increased diversity in the fuel marketplace due to the expansion of biomass-based fuels. The increased use of alternative fuels is being driven predominantly by the Energy Independence and Security Act of 2007 (EISA), which mandates the use of 36 billion gallons of biofuels in the transportation fuel pool by 2022. This is reflected by the fact that more than 95% of U.S. gasoline currently contains ethanol at approximately a 10% level [11]. Addition of ethanol to gasoline comes with some challenges, potentially increasing Reid vapor pressure (RVP), altering distillation characteristics, and preventing transport in pipelines due to risk of water-induced phase separation. The energy content of ethanol is also about one-third less than gasoline on a volume basis. On the other hand, ethanol has both a higher octane number and a higher heat of vaporization than gasoline [12].

In addition to ethanol as a gasoline fuel extender, butanol has received much attention as a second generation biofuel for use in SI engines [2, 13, 14]. Butanol can be produced from biomass sources (biobutanol), including corn, wheat, sugar beet, sorghum, cassava, and sugarcane, as well as agricultural residues, through a fermentation process [15]. Butanol is a higher chain, higher molecular weight alcohol with a four-carbon structure. There are different isomers based on the location of the hydroxyl (OH) group and carbon chain structure. Butanol is less corrosive than ethanol and has a higher energy content than ethanol that is close to gasoline. In comparison to ethanol, butanol has higher tolerance to water contamination, potentially allowing its use of the existing distribution pipelines. Butanol also has an increased octane number compared to gasoline, and lower heat of vaporization compared to ethanol, which would provide cold-start benefits for engines running with butanol blended fuels compared with ethanol blends with gasoline [15, 16].

A number of studies have examined the effect of ethanol content on particle and gaseous emissions in vehicles and engines equipped with DI fueling. Storey et al. [17] found that E10 and E20 blends decreased particle number emissions when they used a turbocharged DI vehicle over different driving cycles. Maricq et al. [18] showed small benefits in PM mass and particle number emissions as the ethanol level in gasoline increased from 0 to 20% when they tested a SI-DI turbocharged vehicle with two engine calibrations. They also found higher reductions in both PM mass and particle number emissions with ethanol contents >30%. Clairotte et al. [19] tested a Euro 5 vehicle with a DI engine over the New European Driving Cycle (NEDC) and the Common ARTEMIS cycles on different ethanol blends and found elevated acetaldehyde and methane emissions and a reduction in toluene and ammonia emissions with increasing ethanol content. Wallner and Frazee [20] found decreased nitrogen oxides (NO_x), total hydrocarbons (THC), and carbon monoxide (CO) emissions with increasing ethanol content, while formaldehyde and acetaldehyde showed an increasing trend.

Butanol has not been studied as extensively as ethanol. Wallner and Frazee [20] utilized n-butanol and iso-butanol as blending agents with gasoline in a DI SI engine. They found that NO_x, CO, and THC emissions were lower with increasing butanol content in gasoline, while some increases were seen for formaldehyde and acetaldehyde emissions. Wallner et al. [21] used pure gasoline, E10, and 10% butanol in a DI SI engine and showed that the butanol blend had lower volumetric fuel consumption and lower NO_x emissions compared with the ethanol blend. Dernotte et al. [22] assessed different butanol-gasoline blends at different engine loads, spark timings, and equivalence ratios in a PFI SI engine. They found some important THC reductions with butanol, while no significant differences were seen in NO_x emissions. Schulz and Clark [23] carried out a study comparing various ethanol blends and a 16% butanol blend using six modern technology vehicles over the FTP cycle. They found a limited number of statistically significant differences between the fuels tested, however, a decreasing trend in CO and formaldehyde emissions was observed with the butanol blend compared to gasoline. Finally, Karavalakis et al. [24] investigated the impact of using E10, E15, E20, 16% iso-butanol, and a mixture consisting of E10 and 8% iso-butanol on three modern PFI SI light-duty vehicles over the FTP and the Unified Cycle. They found that in most cases butanol blends resulted in reductions in THC, CO, and NO_x compared to E10, while some increases were observed for formaldehyde and acetaldehyde. They also showed that iso-butanol blends resulted in higher particle number emissions compared to E15 and E20 blends for some testing combinations.

The goal of this study is to examine how ethanol-gasoline blends and iso-butanol gasoline blends impact the criteria emissions, gaseous air toxic pollutants, and PM emissions from two modern technology light-duty gasoline vehicles fitted with DI stoichiometric engines. Testing was conducting over the Federal Test Procedure (FTP) driving cycle to include the important effects of cold-start and transient operation. The study utilized a total of seven alcohol blends, including E10, E15, E20, Bu16, Bu24, Bu32, and E10/Bu8.

EXPERIMENTAL

Test Fuels and Vehicles

A total of seven fuels were employed in this study. The fuel test matrix included an E10 fuel (10% ethanol and 90% gasoline), which served as the baseline fuel for this study, and two more ethanol blends, namely E15 and E20. For this study, iso-butanol was blended with gasoline at proportions of 16 (Bu16), 24 (Bu24), and 32% (Bu32) by volume, which are the equivalent of E10, E15, and E20, respectively, based on the oxygen content. In addition, an alcohol mixture consisting of 10% ethanol and 8% iso-butanol (E10/Bu8) was used. This mixed alcohol formulation was equivalent to E15 based on the oxygen content. All fuels were custom blended to match the oxygen contents, maintain the Reid vapor pressure (RVP) within certain limits (6.4-7.2 psi), and match the fuel volatility properties, except the E10/Bu8 fuel that was a 50/50 splash blend of the E20 and Bu16 fuels. Some key properties showing that the test fuels of this study were match-blended are illustrated in Figures 1 and 2. The main physicochemical properties of the test fuels are listed in Table A1 (see Appendix).

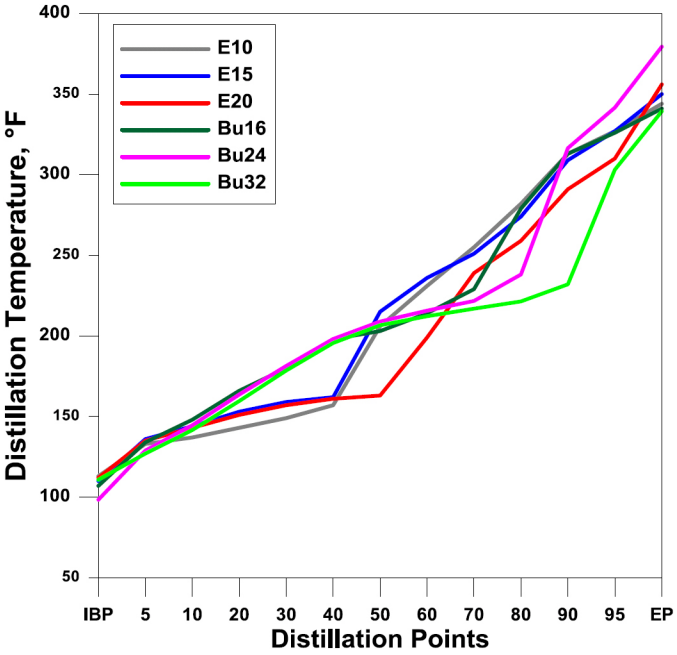


Figure 1. Distillation characteristics for the ethanol and iso-butanol blends.

The test matrix included two 2012 model year (MY) passenger cars equipped with wall-guided direct injection fueling with stoichiometric combustion. Both vehicles were also fitted with a three-way catalyst (TWC). The first vehicle (Kia Optima) was a 2.4 L, 4 cylinders DI engine, having a rated horsepower of 200 hp at 6300 rpm. The second vehicle (Chevrolet Impala) was a 3.6 L, 6 cylinders DI engine, having a rated horsepower of 300 hp at 6500 rpm. The Kia Optima and the Chevrolet Impala had 11,824 and 25,372 miles, respectively, at the start of the test campaign. The Kia Optima was certified to the Federal Tier 2, Bin 2 emission standards, while the Chevrolet Impala was certified to California LEV II, SULEV emission standards. It should be noted that not every vehicle was tested on all fuels. Only the 2012 Kia Optima was tested on the E10/Bu8 mixture.

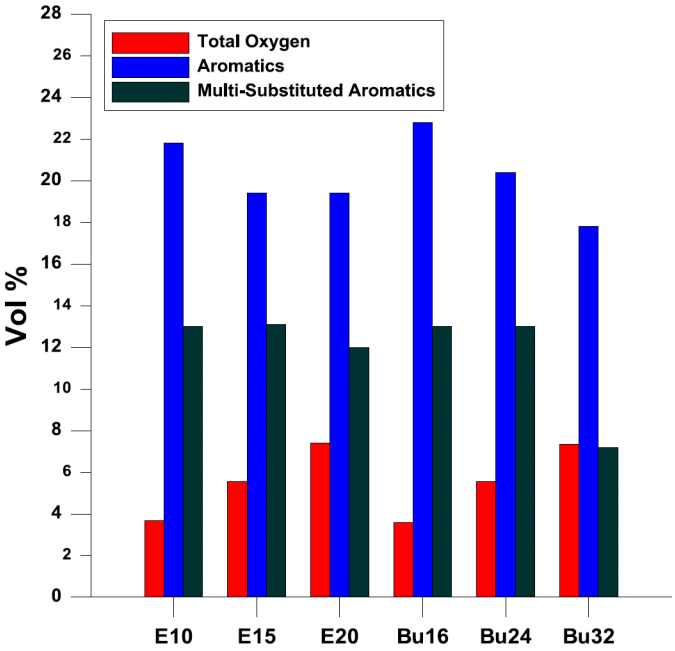


Figure 2. Total oxygen, aromatics, and multi-substituted aromatic contents of the test blends.

Driving Cycle and Measurement Protocol

Each vehicle was tested on each fuel over three Federal Test Procedure (FTP) tests. The three tests on a particular fuel were conducted sequentially once the vehicle was changed to operate on that fuel, and the fuel was not changed to another fuel during this time.

The FTP-75 is the primary emission certification driving cycle of light-duty vehicles in the U.S. The FTP-75 cycle consists of three segments or bags representing a cold-start transient phase, a stabilized phase, and a hot-start transient phase. The cycle covers a total distance of 11.04 miles with an average speed of 21.2 mi/hr. A speed-time trace for the FTP is provided in Figure 3. The vehicle is turned off for a period of 10 minutes at the conclusion of the stabilized phase and prior to starting the hot-start transient phase.

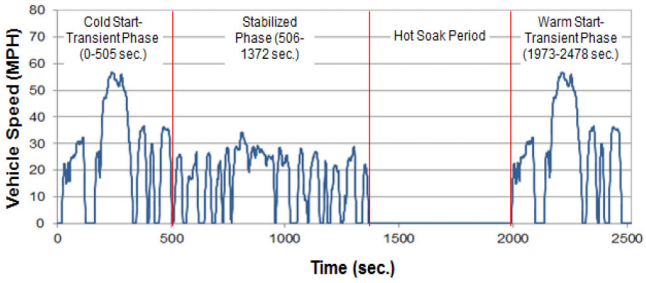


Figure 3. Speed-time profile of the FTP-75 driving cycle.

Prior to testing any particular vehicle, an extensive preconditioning procedure was followed regarding oil and fuel changes. Figure A1 (Appendix) summarizes the oil and fuel

conditioning procedure in a flow chart. Prior to beginning testing on a vehicle, its lubricant oil was changed. Following the oil change, the vehicle was conditioned on the oil over two US06 cycles, followed by an LA4 and a US06 cycle sequence repeated twice (i.e., a total of 4 US06 cycles and 2 LA4s). The vehicle fuel preconditioning procedure incorporated multiple fuel drains and fills to ensure complete changeover of the fuel and to minimize or eliminate carryover effects between test fuels. The preconditioning procedure was similar to that specified in the Code of Federal Regulations (40 CFR 86.132-96). This drain and fill sequence included two drain and 40% fills and one drain and 3 gallon fill. After the drain and 3 gallon fill, and the first drain and 40% fill, the vehicle was then conditioned either on the road or on the dynamometer over the Urban Dynamometer Driving Schedule (UDDS)/LA4, or the first two bags of the FTP. The on-road course was designed to simulate the LA4 portion of the FTP in terms of typical speeds as well as number of stops. In between drain and fill and preconditioning cycles, the vehicle was idled one or two times for two minutes with the vehicle being rocked back and forth. Following the first LA4, a sequence of engine off and idles was performed along with a drain and 40% fill. After this sequence, the vehicle was given its final preconditioning LA4 on the dynamometer, and then placed into cold soak overnight prior to performing the FTP or UC test.

Emissions Testing and Analysis

All tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL), which is equipped with a Burke E. Porter 48-inch single-roll electric dynamometer. A Pierburg Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system was used to obtain certification-quality emissions measurements. For all tests, standard bag measurements were obtained for THC, CO, NO_x, non-methane hydrocarbons (NMHC), and CO_2. NMHC was determined from the combined results from the THC analyzer and a separate CH_4 analyzer. Bag measurements were made with a Pierburg AMA-4000 bench.

PM measurements were made on both a mass and number basis. PM mass samples were collected cumulatively over the entire FTP cycle, with one sample collected for each test. Total PM mass determinations were collected using 47 mm Teflon® filters and measured with a 1065-compliant microbalance in a temperature and humidity controlled clean chamber.

Total particle number was measured using a TSI 3776 ultrafine-Condensation Particle Counter (CPC). This is a butanol-based CPC that has the ability to count particles down to 2.5 nm. This instrument can sample about 300,000 particles per second, making the ultrafine CPC ideal for an accurate total particle number measurement.

Black carbon measurements were taken with a multi-angle absorption photometer (MAAP). The MAAP is a filter-based measurement that uses one light source at 670 nm to produce photons directed towards the particles accumulated on a Teflocarbon filter paper. The back scattering of these photons is then measured by four photo-detectors located at 45 degree intervals. As particles accumulate on the filter paper, the light transmitted back or above the filter paper is correlated to the concentration of black carbon.

Real-time particle size distributions were also obtained for some fuel blends using an Engine Exhaust Particle Sizer (EEPS) spectrometer. The EEPS was used to obtain real time second-by-second size distributions between 5.6 to 560 nm. Particles were sampled at a flow rate of 10 lpm, which is considered to be high enough to minimize diffusional losses. They were then charged with a corona charger and sized based on their electrical mobility in an electrical field. Concentrations were determined through the use of multiple electrometers.

Samples for carbonyl analysis were collected through a heated line onto 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA). Sampled cartridges were extracted using 5 mL of acetonitrile and injected into an Agilent 1200 series high performance liquid chromatograph (HPLC) equipped with a variable wavelength detector. The column used was a 5 µm Deltabond AK resolution (200cm × 4.6mm ID) with upstream guard column. The HPLC sample injection and operating conditions were set up according to the specifications of the SAE 930142HP protocol [25].

Samples for 1,3 butadiene, benzene, toluene, ethylbenzene, and xylenes were collected using Carbotrap adsorption tubes consisting of multi-beds, including a molecular sieve, activated charcoal, and carbotrap resin. An Agilent 6890 GC with a FID maintained at 300 °C was used to measure volatile organic compounds. A Gerstel TDS thermal adsorption unit was used for sample injection. This unit ramps the temperature from 30 °C to 380 °C at a rate of 6 °C per minute to desorb the sample from the tubes. A 60 m × 0.32 mm HP-1 column was used. For these analyses, the GC column and operating conditions were set up according to the specifications of SAE 930142HP Method-2 for C_4-C_{12} hydrocarbons. It should be noted that the amount of sample that is collected and injected into the GC using the Carbotrap absorption tubes is considerably greater than what can be achieved using Tedlar bag samples, since the absorption tubes are sampled over the duration of the test cycle, and hence allow for much large volume of sample to be injected into the GC. 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.

RESULTS AND DISCUSSION

The figures for each emission component show the results for each vehicle tested on the alcohol blends over the FTP driving cycle based on the average of all tests conducted on that particular fuel blend. The error bars represent the standard deviation for the average for each fuel. Statistical comparisons between fuels for a given vehicle were made using a 2-tailed,

2-sample, equal variance *t*-test. For the purpose of this discussion, results are considered to be statistically significant for $p \geq 0.05$.

THC, NMHC, and CH_4 Emissions

Figure 4 presents the THC emissions for all vehicle/fuel combinations over the FTP cycle. In general, THC emissions were found at very low concentrations for both vehicles, ranging from 0.007 to 0.014 g/mile. The largest portion of the THC emissions were emitted during the first 200-300 seconds of the FTP cycle (bag 1) when the engine was cold and the catalyst below its light-off temperature. The Kia Optima showed an increasing trend in THC emissions with increasing ethanol content in the fuel. For the Kia Optima, the increases in THC emissions for E15 (56%, p=0.005) and E20 (92%, p=0.014) blends were statistically significant relative to the baseline E10. No statistically significant differences were seen for THC emissions for the Chevrolet Impala with the exception of E15 blend compared to E10, which showed an increase of 22% (p=0.023) at a statistically significant level. The butanol blends showed an increasing trend compared to E10 for the Kia Optima, with Bu16 (44%, p=0.039) and Bu32 (55%, p=0.020) blends resulting in statistically significant THC increases compared to E10. Similar to E15, a statistically significant increase in THC emissions was found for the E10/Bu8 (33%, p=0.043) alcohol mixture compared to E10. No statistically significant differences were observed for the butanol blends compared to E10 for the Chevrolet Impala.

NMHC emissions are shown in Figure 5. NMHC emissions followed similar patterns with THC emissions for both vehicles. For the Kia Optima, E15 (48%, p=0.007) and E20 (85%, p=0.005) blends produced statistically significant increases in NMHC compared to E10, while for the Chevrolet Impala only the E15 (26%, p=0.044) blend showed a statistically significant increase compared to E10. For the Kia Optima, most butanol blends, including the E10/Bu8 mixture, exhibited some increases in NMHC emissions compared to the E10 blend, with Bu32 (42%, p=0.030) showing an increase in NMHC emissions at a statistically significant level. For the Chevrolet Impala, the butanol blends did not show any strong fuel trends in terms of NMHC emissions and remained at the same levels as the E10 blend.

Trends of decreasing THC/NMHC emissions with increasing alcohol concentration have generally been seen in previous studies utilizing test cell engines or larger fleets of older technology vehicles [14, 23, 26, 27]. This phenomenon has been widely attributed to the presence of oxygen content in the fuel, which leans the air-fuel ratio and promotes oxidation during combustion and over the catalyst. On the other hand, some increases in THC/NMHC emissions with ethanol and butanol fuels have been observed in previous studies conducted in test cell engines and light-duty vehicles [22, 28]. Under the present test conditions, it was hypothesized that the fuel oxygen content played a rather small role in the increase of THC/NMHC emissions; the increase in THC/NMHC emissions was likely due to fuel impingement on combustion chamber surfaces. It is therefore reasonable to assume that a portion of THC emissions might derived from unburned fuel fractions after the first seconds of the FTP cycle (cold-start). It is also interesting to note that in most cases the THC emissions for the butanol blends, especially B24 and B32, were found to be lower compared to those of E15 and E20 blends. This reduction in THC emissions with the higher butanol blends relative to the higher ethanol blends could be due to the lower latent heat of vaporization of iso-butanol compared to ethanol.

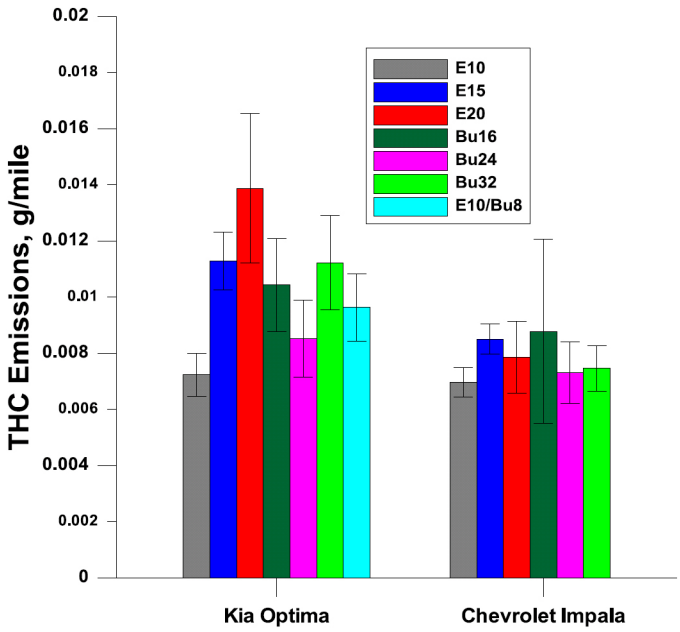


Figure 4. THC emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

Methane is emitted from light-duty vehicles due to the incomplete combustion of fuel in the engine and the incomplete oxidation of engine-out CH_4 over the catalyst. Although CH_4 is not toxic and not relevant to ozone-forming processes, it is a potent greenhouse gas. Figure 6 shows the CH_4 emissions for all vehicle/fuel combinations over the FTP cycle. Overall, CH_4 emissions were at very low levels for both vehicles, ranging from 0.001 to 0.003 g/mile. For the Kia Optima, most alcohol blends showed an increase in CH_4 emissions compared to E10, with E15 (57%, p=0.003), E20 (93%, p=0.050), and Bu32 (90%, p=0.034) showing statistically significant differences. For the Chevrolet Impala, there was a lack of strong trends in CH_4 emissions, with the exception of Bu24 blend, which showed a statistically significant increase of 54% (p=0.046) compared to E10. Generally, the use of alcohol fuels can limit the main CH_4-forming pathways. This is because the precursors of CH_4 formation are CH_3 and C_8H_{18}, which their contribution to produce CH_4 is decreased when an alcohol fuel is added to gasoline. Under the present test conditions some higher ethanol and butanol blends showed higher CH_4 emissions compared to E10. This finding indicates that the excess CH_4

emissions can hardly compensate for the potential benefits of ethanol and butanol fuels considering the global warming potential of CH_4 (21 eq pounds CO_2 over 100 years).

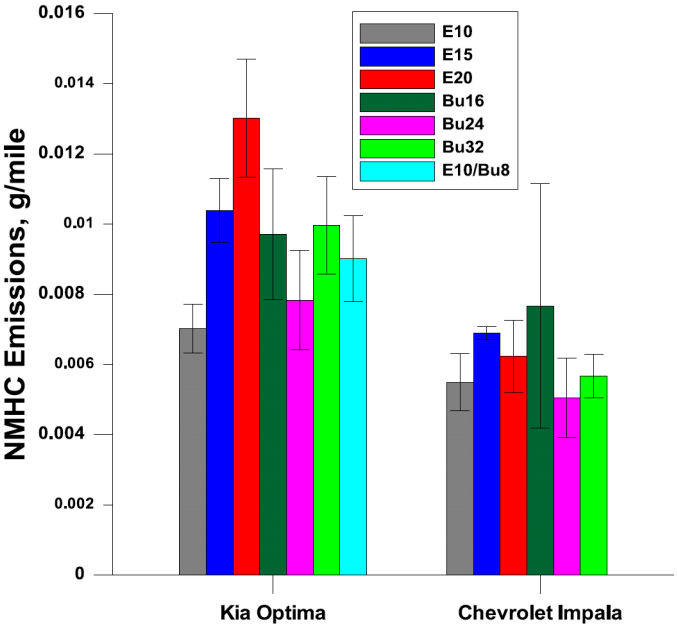


Figure 5. NMHC emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

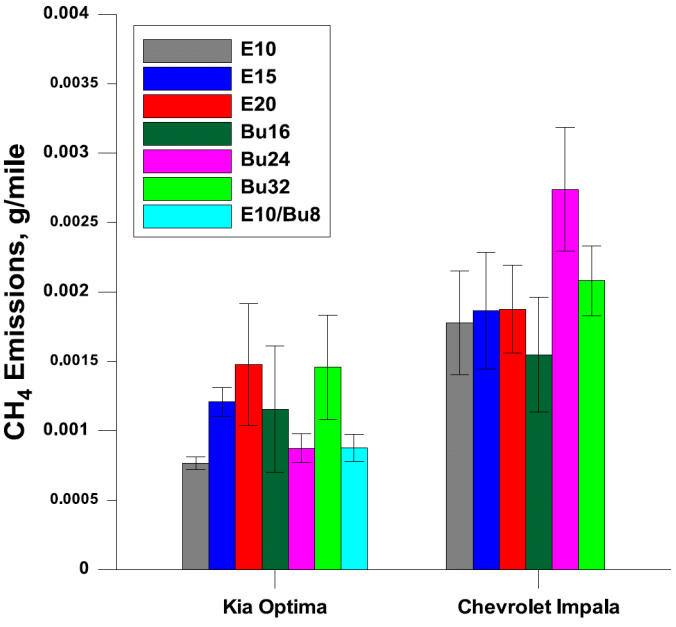


Figure 6. CH_4 emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

CO Emissions

Emissions of CO are shown in Figure 7. CO emissions showed mixed results for both vehicles, with both increases and decreases. No statistically significant differences were seen between the fuels tested for both vehicles. This result was as expected since both engines use stoichiometric combustion and tightly control the global equivalence ratio close to 1.0, producing little CO emissions and relatively minor changes in air-fuel ratio throughout the testing. Note that CO emissions for both vehicles were found to be significantly lower than the applicable EPA emission standards (1.0 g/mile).

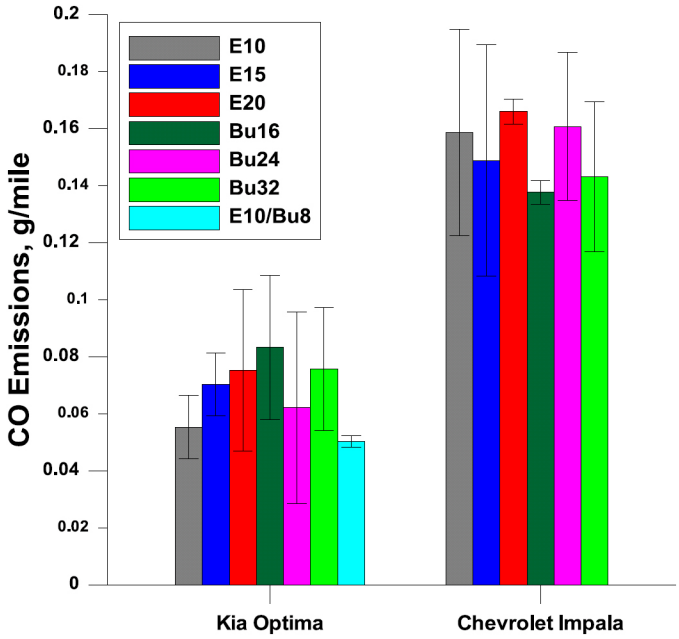


Figure 7. CO emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

NO_x Emissions

Figure 8 shows the variation of NO_x emissions according to the ethanol and iso-butanol content for the test vehicles over the FTP cycle. NO_x emissions were found to be higher for the Chevrolet Impala than the Kia Optima, which trends with the lower THC emissions for the Chevrolet Impala. For the Kia Optima, NO_x emissions did not show any significant differences between the fuels. For the Chevrolet Impala, the only statistically significant increase in NO_x emissions compared to the baseline E10 was seen for Bu32 blend (29%, p=0.013). Both vehicles exhibited lower NO_x emission levels than the applicable EPA emission standards (0.02 g/miles).

Previous studies have shown that NO_x emissions can increase with low, intermediate, and higher ethanol blends, although this trend is not consistent between studies and is stronger in older vehicles [26],[27, 29]. Other studies have also shown that NO_x emissions can decrease with the addition of butanol [30]. However, most of these studies have utilized PFI engines or vehicles, whereas the present investigation is employing modern technology DI vehicles. It has been reported that NO_x emissions with increasing ethanol or butanol content in gasoline in a DI engine can be reduced due to the increased heat of vaporization of ethanol and butanol as compared to gasoline, resulting in a lower in-cylinder temperature at the end of compression [10].

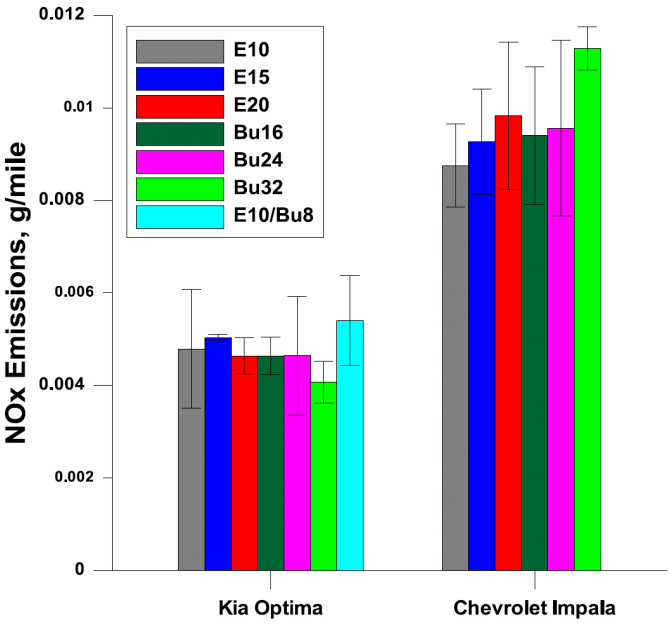


Figure 8. NO_x emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

CO_2 Emissions and Fuel Economy

Figure 9 shows the effect of alcohol type and concentration on the CO_2 emissions for the test vehicles over the FTP cycle. CO_2 emissions showed some specific differences between different fuels for the different vehicles, but no consistent trends over all testing conditions. For the Kia Optima, CO_2 emissions were found to be lower at a statistically significant level for E20 (1%, p=0.024) and Bu32 (2%, p=0.038) but higher for E10/Bu8 (2%, p=0.020) compared to E10 blend. For the Chevrolet Impala, a decreasing trend was seen in CO_2 emissions for the higher ethanol and all butanol blends compared to E10, with the exception of E15. The highest reduction in CO_2 emissions was observed for Bu24 blend (2%, p=0.036) compared to E10, which was also statistically significant. The reductions in CO_2 emissions with the alcohol blends could be ascribed to the presence of oxygen atoms in the fuel, which favors the carbon oxidation process in CO and CO_2.

Fuel economy results for the test vehicles over the FTP cycle are presented in Figure 10. For this study, fuel economy was calculated based on the carbon balance method and the unique properties for each different test fuel and not according to the standard EPA equation. The carbon balance equation more directly accounts for the differences in energy content between different fuels, which are somewhat normalized out in the standard EPA equation. Overall, the results revealed that as the alcohol concentration increased the fuel economy decreased approximately proportionally to the decrease in energy content of the blend. This trend was consistent for both vehicles, with the higher ethanol blends and butanol blends showing lower fuel economy than E10 and Bu16, respectively, while the E10/Bu8 blend had about the same fuel economy as the E15 blend. For the Kia Optima, statistically significant reductions in fuel economy were seen for E15 (2%, p=0.007) and E20 (3%, p=0.002) compared to E10, and Bu24 (3%, p=0.040) and B32 (4%, p=0.006) compared to Bu16. The E10/Bu8 blend showed a statistically significant reduction in fuel economy relative to both E10 (4%, p=0.003) and Bu16 (6%, p=0.001) blends. For the Chevrolet Impala, E15 and E20 blends exhibited fuel economy statistically significant reductions of 4% (p=0.038) and 3% (p=0.009), respectively, compared to E10, while only Bu32 blend showed a decrease of 4% (p=0.026) in fuel economy at a statistically significant level compared to Bu16 blend.

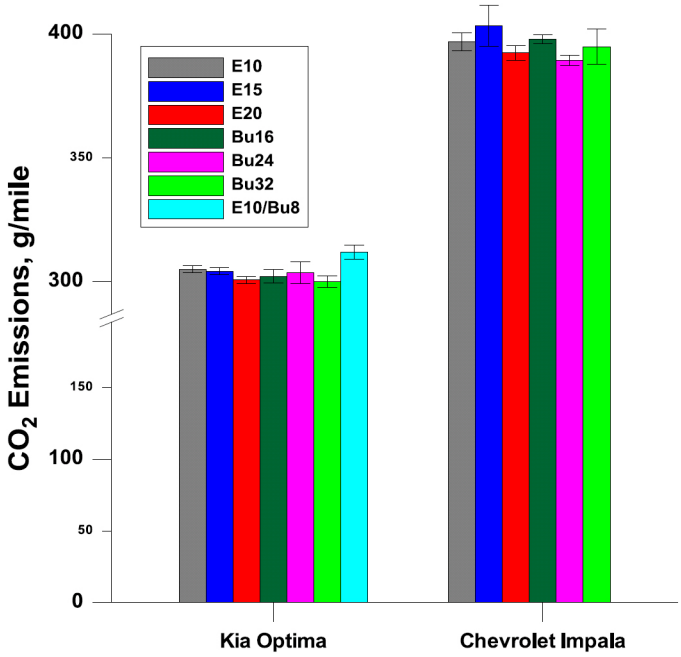


Figure 9. CO_2 emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

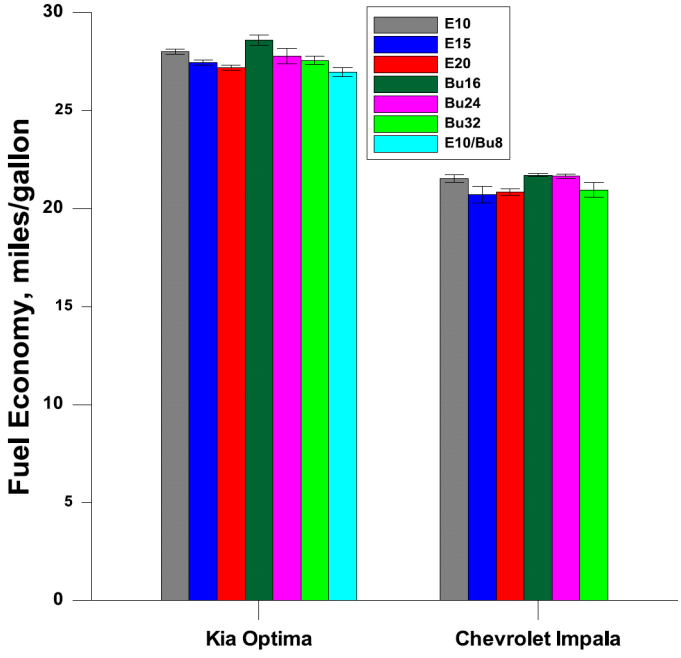


Figure 10. Fuel economy for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

PM Mass, Particle Number Emissions, and Black Carbon Concentrations

The cumulative PM mass emissions are shown in Figure 11. PM emission results were as expected; in most cases, PM mass trended lower with an increase in the oxygen content in the fuel. Other properties, such as fuel volatility, can also play a role in PM emissions, which is sometimes more important than the presence of oxygen in the fuel. However, in the current study most physicochemical properties of the test fuels were kept constant with relatively narrow ranges. Thus, the oxygen content should be the primary contributing factor for lowering PM emissions. Separating the alcohol types, for the Kia Optima, there is a marginal reduction in PM mass emissions for E15 and E20 blends compared to E10. Looking at the butanol blends, the reductions in PM mass emissions were more pronounced with Bu24 and Bu32 blends showing statistically significant decreases in PM emissions in the order of 33% (p=0.005) and 75% (p=0.00001), respectively, compared to Bu16. The E10/Bu8 mixture showed statistically significant decrease in PM mass emissions from both E10 (28%, p=0.001) and Bu16 (56%, p=0.00002) blends. It should be noted that Bu16 exhibited significantly higher PM mass emissions compared to all other alcohol blends. In particular, there was a 64% (p=0.0001) increase in PM emissions for Bu16 relative to E10, although both fuels have the same oxygen content.

For the Chevrolet Impala, the PM mass results showed some trends with the oxygen content in the fuel, with the E20 and Bu32 fuels showing the lowest PM mass levels. The E20 fuel showed a statistically significant decrease in PM relative to E10 on the order of 50% (p=0.018). E10 and E15 produced about the same PM mass emissions. The butanol blends did not exactly follow the same trends as those observed for the Kia Optima, with Bu24 exhibiting a statistically significant 34% (p=0.026) increase in PM mass emissions relative to Bu16. A statistically significant reduction in PM emissions in the order of 55% (p=0.007) for B32 relative to Bu16 was also seen.

For this study, PM mass results ranged from 1.14 to 7.11 mg/mile, averaging at about 4.21 mg/mile for the Kia Optima and at 2.52 mg/mile for the Chevrolet Impala. While this study employed relatively modern vehicles, it appears that additional reductions in PM emissions will be needed to meet the future California LEV III and Tier 3 standards for PM mass emissions to be implemented by 2021 (3 mg/mile), and in particular the even more stringent LEV III PM mass standards for 2025 (1 mg/mile). The high PM mass emissions for the SI DI fueled vehicles are considered to be typical behavior and have been reported in previous studies [6, 31, 32]. Elevated PM mass emissions from SI DI vehicles are predominantly released from the cold-start phase where cold piston and cylinder surfaces exacerbate liquid fuel impingement and reduce evaporation from surfaces, which produces soot when the fuel ignites.

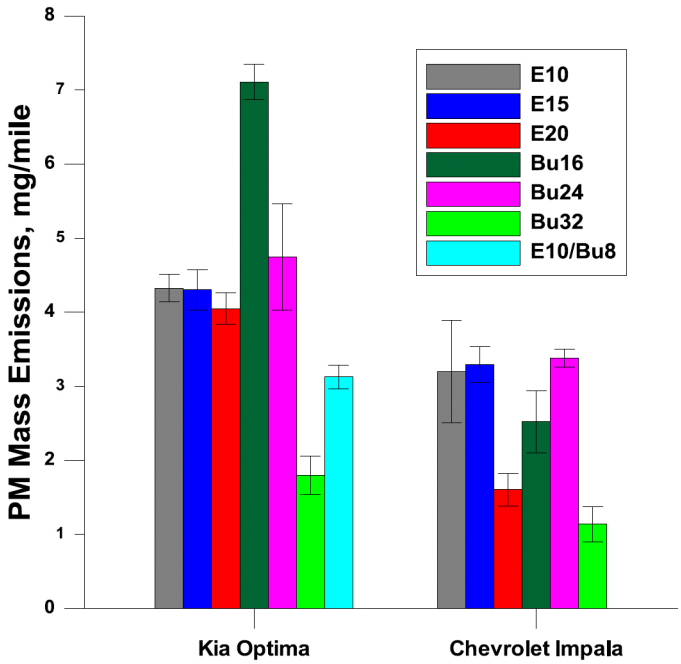


Figure 11. PM mass emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

The total particle number emissions are displayed in Figure 12a. Particle number emissions corroborate the PM mass trends, with the Kia Optima generally showing higher particle number emissions than the Chevrolet Impala. For the Kia Optima, the blends of E15 and E20 exhibited statistically significant decreases in particle number emissions of 23 and 30%, respectively, compared to E10. Analogous to ethanol blends, statistically significant decreases in particle number emissions were also seen for Bu24 (34%) and Bu32 (72%) blends relative to Bu16. The alcohol mixture (E10/Bu8) showed a statistically significant reduction in particle number emissions from both E10 (22%) and Bu16 (47%) blends, respectively.

For the Chevrolet Impala, particle number emissions showed mixed results. Particle number emissions for E10, E15, and E20 were not significantly different. For the butanol blends, there was a 46% increase in particle number emissions for Bu24 relative to Bu16 at a statistically significant level. A sharp reduction for Bu32 in the order of 39% compared to Bu16 was also observed at a statistically significant level.

Particle number results reported here generally decreased with the addition of ethanol and iso-butanol, implying that the presence of oxygen in the fuel was the main contributing factor for the particle number decrease by suppressing soot formation. In addition to the oxygen content, particles are also strongly related to the aromatic hydrocarbons content in the fuel. The addition of higher blends of ethanol and iso-butanol in gasoline decreased the fraction of aromatic hydrocarbons and

therefore their propensity of forming soot. This is consistent with the findings of Wallner and Frazee [20], which showed that the reduced carbon available in ethanol combustion decreases the potential for benzene and soot formation as the ethanol blend ratio increases. It is interesting to note that the iso-butanol blends had higher particle number emissions compared to their corresponding ethanol blends, with the exception of Bu32, which emitted the lowest particle number emissions for both vehicles. This phenomenon could be attributed to the fact that during SI DI combustion branched butanols can produce intermediate products, such as propene and butene, leading to the formation of more benzene and soot [33]. The results of this study indicate that the degree of branching (iso-butanol versus ethanol) may have a stronger impact on soot formation than the oxygen content, since the butanol blends had equivalent oxygen contents to their corresponding ethanol blends. In addition to fuel structure, the higher viscosity of butanol blends relative to ethanol blends could also influenced particle number emissions by altering the fuel spray characteristics.

Figure 12 (b-c) the particle number emissions for the individual bags of the FTP cycle for the Kia Optima and Chevrolet Impala, respectively. The results show that a major amount of particle number counts is emitted in the early phase of the FTP (phase 1 or bag 1) when the engine is cold and the TWC is below its light-off temperature. The sharp increases in particle number emissions during cold-start could be due to fuel accumulation onto the cold piston and cylinder surfaces. For phase 2 and phase 3 of the FTP cycle, particle number emissions were substantially lower than those of phase 1. For bags 2 and 3, the significant reduction in the PN emissions can be attributed to the higher intake air temperature, fuel temperature, and piston surface temperature promote fuel vaporization and thus better fuel-air mixing coupled with the higher efficiency of the TWC once it has reached its light-off temperature [34].

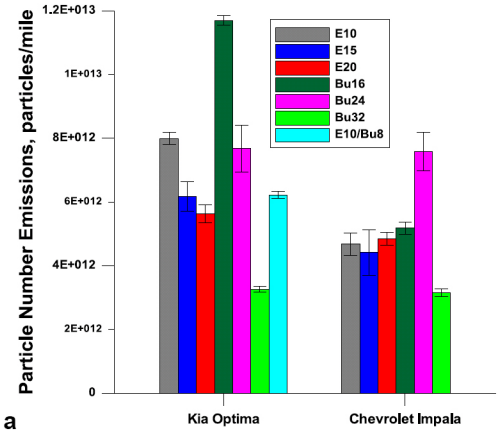
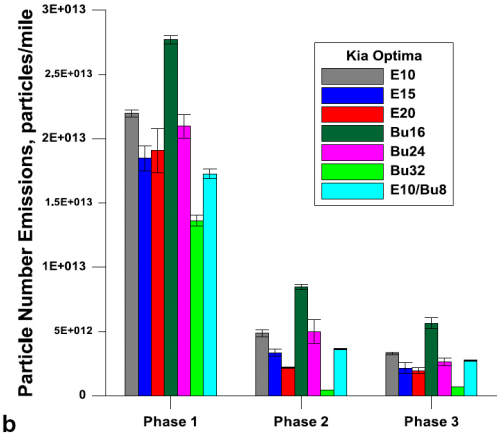


Figure 12.



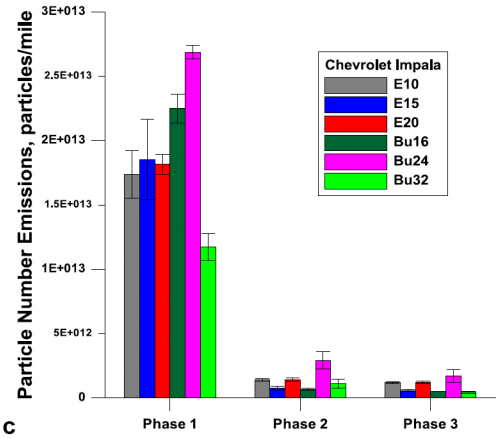


Figure 12 (a-c). (cont.) Total particle number emissions for all vehicle/fuel combinations over the FTP cycle (a) and particle number emissions by phase for the Kia Optima (b) and the Chevrolet Impala (c). Errors bars represent ± one standard deviation around the average value for each fuel.

Figure 13 presents the black carbon concentration results over the FTP cycle. It should be mentioned that due to experimental issues the MAAP wasn't available for Bu32 for the Kia Optima and for Bu16 and Bu24 for the Chevrolet Impala.

Black carbon concentration is an operationally defined quantity that corresponds to the extent to which particles deposited on a filter absorb light. It is generally formed through incomplete combustion. Besides its direct effect on visibility, black carbon also influences the climate on a global and regional scale and public health. Black carbon is known to contribute a positive radiative forcing in the atmosphere through absorption of radiation, but can contribute an indirect negative radiative forcing through the seeding of clouds. It has been suggested that reducing black carbon emissions via reductions in black carbon number concentration will result in a decrease in global cloud radiative forcing [35, 36].

For the Kia Optima, black carbon emissions did not show consistent fuel trends, with only the E15 blend showing a 20% increase relative to E10 at a statistically significant level. For the Chevrolet Impala, the higher ethanol blends led to statistically significant reductions in black carbon emissions relative to E10 in the order of 39 and 34%, respectively, for E15

and E20 blends. Important reductions in black carbon emissions at a statistical significant level were also seen for Bu16 (44%) compared to E10, which was quite surprising because both fuels had similar oxygen contents. Overall, the reductions in black carbon with increasing alcohol content in the fuel could be due to the presence of higher oxygen content, which can reduce the tendency to form soot.

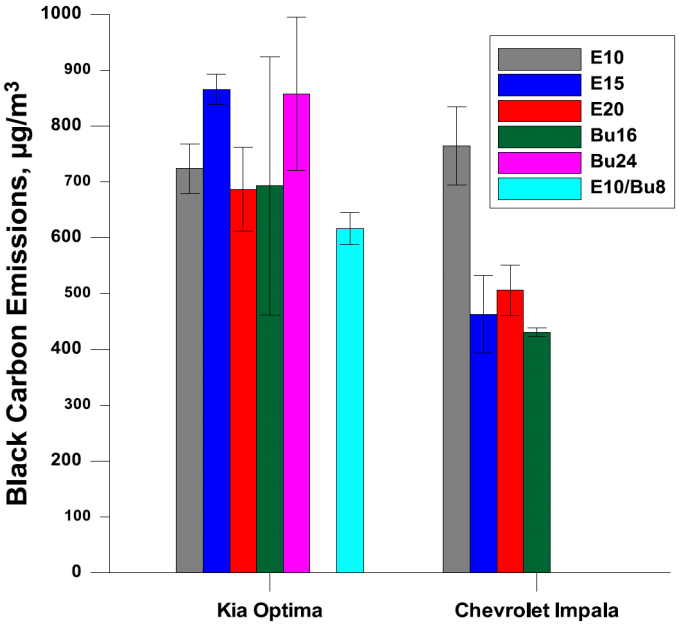


Figure 13. Black carbon emissions for all vehicle/fuel combinations over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

Particle Size Distributions

Real-time particle size distributions were obtained with an EEPS over the FTP cycle. The EEPS wasn't available through the entire course of this study and, therefore, real-time particle size distributions were only obtained for E15, E20, Bu16, and Bu32 for the Kia Optima and for Bu16, Bu24, and Bu32 for the Chevrolet Impala. Figure 14 and Figure 15 present the size distributions for the Kia Optima and Chevrolet Impala, respectively. Overall, the fuel effect was particularly noticeable in particle size distributions for the Kia Optima, with the higher oxygen content blends exhibiting decreases in the number concentration of particles. Some trends were also seen for lower accumulation mode particles with decreasing aromatics content. These results suggest that the sooting tendency decreases with increasing oxygen content and decreasing aromatics.

Both SI DI vehicles displayed diesel-like distributions that were unimodal in nature. The particle size distributions for all test fuels were dominated by the accumulation mode particles, which are formed by agglomeration of nucleation mode particles and may also include condensed or adsorbed volatile material. This finding is consistent with previous studies conducted with SI DI vehicles on oxygenated fuel formulations [17, 34, 37]. The accumulation mode geometric number mean diameter for all fuels and both vehicles ranged from ~60 nm to 90 nm. For the Kia Optima, the geometric number mean diameter for E15 was higher (~80 nm) than E20 (~69 nm), possibly due to the higher concentrations of particles that result in more coagulation. Comparing the butanol blends, the mean diameter for Bu16 (~93 nm) was higher relative to Bu32 (~70 nm). Overall, Bu16 showed sharp increases in accumulation mode particles compared to the other blends, with Bu32 exhibiting the lowest accumulation mode particles. The higher concentration particles for Bu16 are consistent with the much higher PM mass and total particle number emissions observed for this blend over the entire FTP. In general, the particle size distribution results for the Kia Optima agree well with the PM mass and particle number emissions. It should be mentioned that our results for Bu16 do not agree with those reported in a previous study showing that a 12% iso-butanol blend produced lower accumulation mode particles than E10 and E20 [38]. The discrepancies between the present study and the study conducted by He et al. [38] could be due to the fact that the latter work was performed on an engine dynamometer and more importantly the fuels used were splash blended.

For the Chevrolet Impala, accumulation mode particle concentrations were found to be substantially lower than those of the Kia Optima. This observation is in agreement with the lower PM mass and total particle number counts for the Chevrolet Impala compared to Kia Optima. The geometric number mean diameter for Bu24 was similar to Bu16, peaking at around 70 nm, and higher compared to Bu32 (~55 nm). Unlike the size distributions observed for the Kia Optima, Bu24 produced higher accumulation mode particle concentrations followed by Bu16 and Bu32. It should be noted that the results reported here are consistent with the PM mass and particle number emissions seen for the Chevrolet Impala.

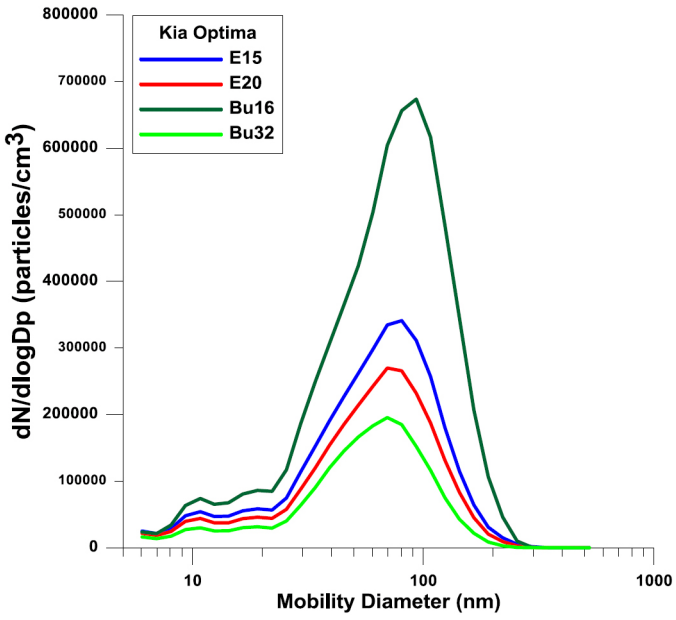


Figure 14. Average particle size distribution results for the Kia Optima over the FTP cycle.

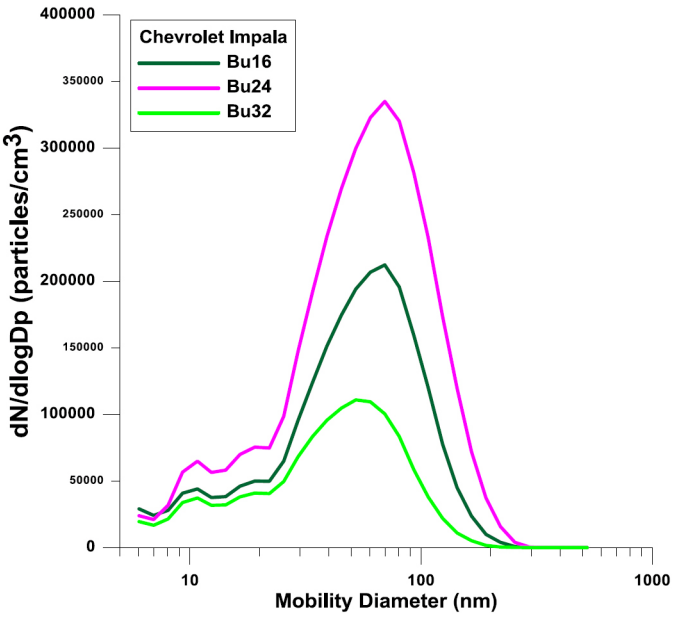


Figure 15. Average particle size distribution results for the Chevrolet Impala over the FTP cycle.

Carbonyl Emissions

This study was able to identify and quantify thirteen aldehydes and ketones in the exhaust of both vehicles when operated with alcohol formulations. Figure 16 and Figure 17 show the carbonyl emissions for the Kia Optima and Chevrolet Impala, respectively, expressed in mg/mile. For both SI DI vehicles, formaldehyde and acetaldehyde were the most abundant compounds in the tailpipe followed by butyraldehyde, benzaldehyde, crotonaldehyde, methacrolein, and propionaldehyde. Other carbonyl compounds were also present in the exhaust but in lesser amounts, including those of MEK, valeraldehyde, and hexanaldehyde. Hexanaldehyde was detected in small concentrations for some fuel blends and its mainly decreased by the addition of oxygenates in gasoline. Tolualdehyde was undetectable for all fuel blends and for both test vehicles.

Acetaldehyde is classified as probably carcinogenic whereas formaldehyde is classified as human carcinogen by the U.S. Department of Health and Human Services. For both vehicles, a clear reduction in formaldehyde and acetaldehyde emissions was observed with E15 relative to E10. For the Chevrolet Impala, an increase in both formaldehyde and acetaldehyde emissions was seen for E20 relative to E10 blend but not at a statistically significant level. On the contrary, for the Kia Optima, E15 and E20 blends showed marked and statistically significant reductions in both formaldehyde and acetaldehyde emissions relative to E10. For formaldehyde, these reductions were 74 and 88% for E15 and E20, respectively, while for acetaldehyde the reductions were 72 and 82% for E15 and E20, respectively.

For the Kia Optima, the use of Bu24 resulted in higher formaldehyde and acetaldehyde emissions than Bu16 and both E15 and E20 blends. For formaldehyde emissions, the increase for Bu24 relative to Bu16 was 93% and also statistically significant. The use of Bu32 blend clearly led to decreases in formaldehyde and acetaldehyde emissions compared to Bu16, with the difference in formaldehyde emissions being statistically significant. The alcohol mixture E10/Bu8 exhibited similar formaldehyde and acetaldehyde emission levels with the E10 blend. For the Chevrolet Impala, the higher butanol blends showed some decreases in formaldehyde and acetaldehyde emissions compared to Bu16, but not at a statistically significant level.

Generally, gasoline fuels do not contain carbonyl compounds, with the emissions of aldehydes and ketones being a result of partial oxidation of the fuel components during combustion. Previous studies have shown that the addition of ethanol fuels can produce higher formaldehyde and acetaldehyde emissions [24, 39, 40]. Formaldehyde is produced from oxygenated fuels and also by the decrease of fuel aromatics since these compounds do not participate in the formation of formaldehyde [41]. Acetaldehyde is principally produced through the partial oxidation of ethanol. In the case of butanol fuels, acetaldehyde can also be formed via β-scission of aC_4H_8OH [42]. McEnally and Pfefferle [33] showed that branched butanols through their fission produce hydroxyl-ethyl radicals, which likely dissociate by β-scission of the O-H bond to produce acetaldehyde. Formaldehyde can be produced from simple fission followed by β-scission, which produces both an alkane and the aldehyde. Grana et al. [43] showed that the mole fraction of acetaldehyde is lower in the iso-butanol flame, which implies that there is a pathway such that butanol fuels destroy acetaldehyde and then create formaldehyde as indicated by the results of this study.

As expected, butyraldehyde emissions appeared to be higher with the use of higher iso-butanol blends. For both vehicles, the butanol blends and the alcohol mixture (E10/Bu8) showed higher butyraldehyde emissions than the ethanol blends. It should be noted that the differences in butyraldehdye emissions between the butanol blends were not statistically significant. Some statistically significant increases in butyraldehyde emissions were seen between Bu32 and some ethanol blends, however. It was assumed that butyraldehyde was formed via H-atom abstraction of one of the decomposition products of iso-butanol. Benzaldehyde, which is primarily produced from fuel aromatic hydrocarbons, showed mixed trends with the alcohol fuels for both vehicles. For the Kia Optima, benzaldehyde emissions for E15 were higher relative to E10, while E20 was lower. The alcohol mixture was at about the same levels with those of E15. For the butanol blends, some increases in benzaldehyde emissions were seen for Bu24 relative to Bu16, but not for Bu32. Overall, the differences in benzaldehyde emissions for the Kia Optima were not statistically significant and the measurements characterized by large variability. For the Chevrolet Impala, both higher ethanol blends trended lower in benzeldehyde emissions compared to E10. Similar to ethanol blends, the higher butanol

blends showed decreased benzaldehyde emissions compared to Bu16, but not at a statistically significant level. Our results are in agreement with those showing that the addition of oxygenates decrease benzaldehyde emissions [17, 27, 39], but also consistent with other studies showing some increase in benzaldehyde emissions probably because of the enhancement of aromatics oxidation [41, 44]. We hypothesized that benzaldehyde can be produced from oxygen addition to alkyl branchs of toluene, xylene, and trimethylbenzene present in gasoline.

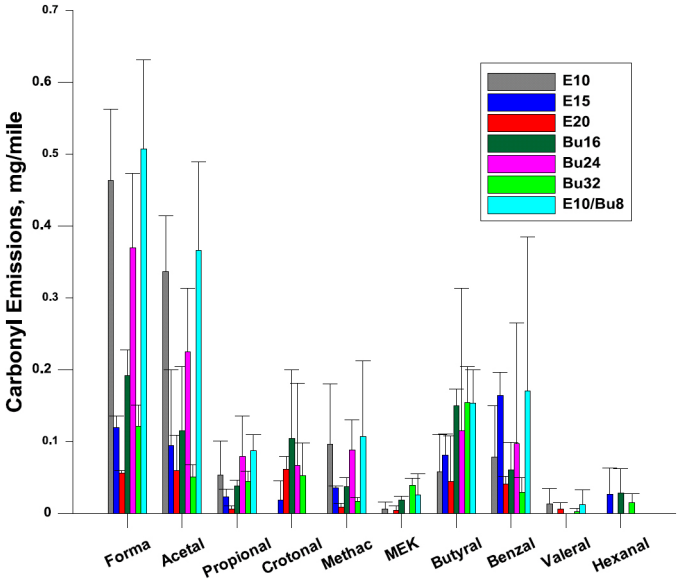


Figure 16. Individual carbonyl compounds for the Kia Optima over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

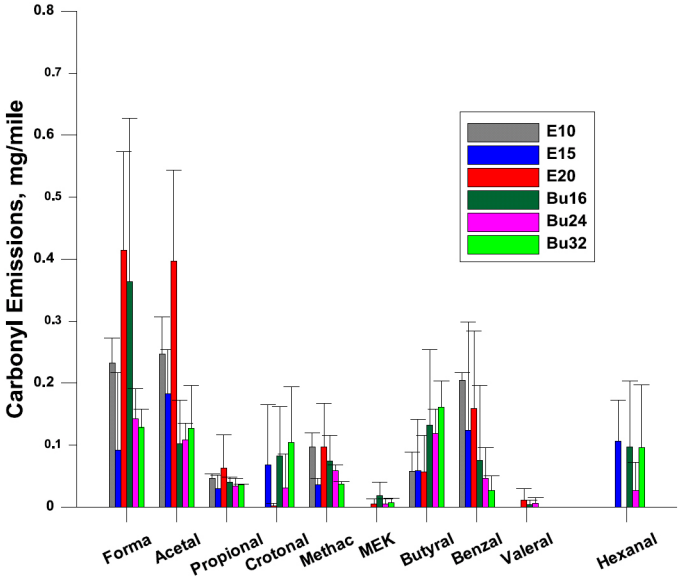


Figure 17. Individual carbonyl compounds for the Chevrolet Impala over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

1,3-Butadiene and BTEX Emissions

Figure 18 and 19 show the cumulative 1,3-butadiene, benzene, ethylbenzene, toluene, *m,p*-xylene, and *o*-xylene emissions over the FTP cycle for the Kia Optima and the Chevrolet Impala, respectively. These emissions were measured cumulatively over the entire cycle and were not weighted like the traditional regulated gaseous emissions. The aromatic hydrocarbons of benzene, ethylbenzene, toluene, *m,p*-xylene, and *o*-xylene are usually termed as BTEX. The most reactive volatile organic compounds (VOCs) from internal combustion engines are BTEX compounds, since they contain a C=C bond, that can add free radicals. In general, BTEX emissions for the Kia Optima were found significantly higher than those for the Chevrolet Impala, following similar trends with the THC emissions for these vehicles.

Overall, 1,3-butadiene and BTEX emissions did not follow a uniform trend for both vehicles and showed both increases and decreases with the use of oxygenated fuels. For the Kia Optima, E15 and E20 increased 1,3-butadiene emissions by 53% and 199%, respectively, relative to E10 blend, with the increase for E20 being statistically significant. This is an important finding since 1,3-butadiene is one of the air toxics of interest and a recognized human carcinogen. The butanol blends did not show statistically significant differences between the fuels. In contrast to the results observed for the Kia Optima, for the Chevrolet Impala 1,3-butadiene emissions trended lower for E15 and E20 relative to E10 but not at a statistically significant level. A statistically significant increase in 1,3-butadiene emissions was observed for Bu24 (56%) relative to Bu16. For the Chevrolet Impala, all butanol blends showed higher 1,3-butadiene levels compared to the ethanol blends.

Benzene is one of the major toxic species emitted in tailpipe emissions and a suspected carcinogen. Some increases were seen for both vehicles in benzene emissions with the use of higher ethanol blends. This phenomenon was more pronounced for the Kia Optima where the increase in benzene emissions for E15 and E20 relative to E10 were 47% and 112%, respectively, and also statistically significant. For the Chevrolet Impala, there was a statistically significant 69% increase in benzene emissions for E15 compared to E10, whereas E20 produced similar levels of benzene emissions with E10 blend. For the butanol blends, Bu24 exhibited a statistically significant decrease of 50% in benzene emissions relative to Bu16 for Kia Optima, whereas for Chevrolet Impala Bu24 showed an increase in benzene emissions of 39% relative to Bu16, which wasn't statistically significant. The blend of Bu32 showed a decrease in benzene emissions relative to Bu16 for both vehicles but not at a statistically significant level. The alcohol mixture emitted similar levels of benzene emissions with E10 and was also found statistically significant lower than Bu16.

Ethylbenzene showed the highest emissions among the target air toxics for all vehicles/fuel combinations. For the Kia Optima, ethylbenzene emissions showed a marked increase for E15

(148%) and E20 (136%) blends compared to E10 at a statistically significant level. A statistically significant reduction in ethylbenzene emissions was seen for Bu24 (43%) relative to Bu16, but not for Bu32. The alcohol mixture was found to be lower at a statistically significant level compared to E15 and Bu16. For the Chevrolet Impala, ethylbenzene emissions did not show any strong trends between the ethanol blends. For the butanol blends, no significant trends were seen in ethylbenzene emissions with the exception of Bu32, which was statistically significant lower than Bu24.

Toluene emissions exhibited some increase with E15 (117%) and E20 (224%) compared to E10 for the Kia Optima. The increase in toluene emissions for E20 relative to E10 was statistically significant. The higher butanol blends, on the other hand, trended lower compared to Bu16 but not at a statistically significant level. As expected, toluene emission levels for E15 and E10/Bu8 were about the same for the Kia Optima. For the Chevrolet Impala, the higher ethanol blends did not show any strong trends in toluene emissions. Similar to the ethanol blends, Bu16 and Bu24 exhibited similar levels of toluene emissions, while Bu32 resulted in lower toluene emissions compared to Bu16. It was expected that a reduction in toluene emissions would have occurred with increasing oxygen content and with the reduction in aromatics content in the fuel. The results of this study indicate that toluene may have a different production pathway in SI DI engines other than through the aromatics in the fuel.

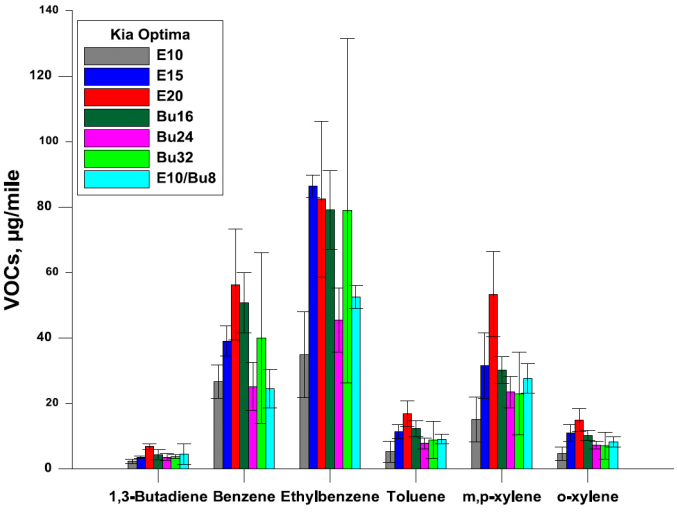


Figure 18. 1,3-Butadiene and BTEX emissions for the Kia Optima over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

Xylene emissions followed similar patterns with toluene emissions for both vehicles. For the Kia Optima, E15 and E20 trended higher than E10, with E20 showing a statistically significant increase in m/p/o-xylenes emissions. Higher xylene emissions were also seen for the E10/Bu8 blend relative to E10 at a statistically significant level with E10/Bu8 having about the same emission levels as E15. The higher butanol blends trended lower in xylene emissions but not at a statistically significant level. For the Chevrolet Impala, the ethanol blends did not present any significant fuel trends, while an overall reduction in xylene emissions was seen for Bu32 compared to Bu16.

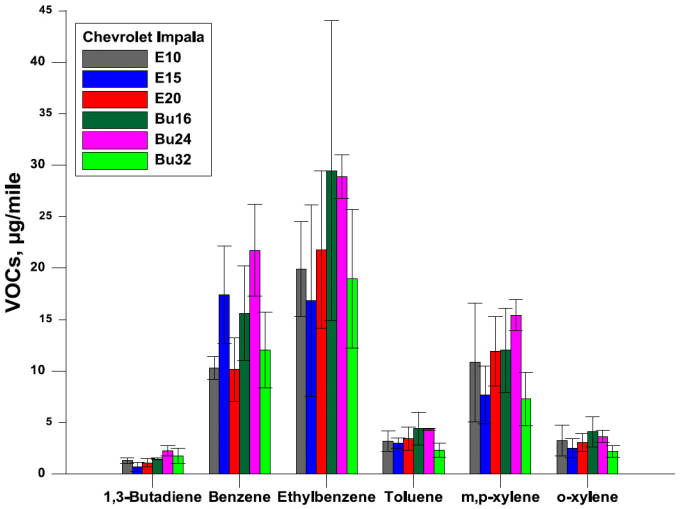


Figure 19. 1,3-Butadiene and BTEX emissions for the Chevrolet Impala over the FTP cycle. Errors bars represent ± one standard deviation around the average value for each fuel.

SUMMARY/CONCLUSIONS

This study, examines the effect of fuel formulation on the criteria emissions, gaseous air toxic pollutants, and particle emissions from two modern technology gasoline passenger cars equipped with direct injection fueling. A total of seven alcohol fuel formulations were utilized, including ethanol blends (E10, E15, and E20), iso-butanol blends (Bu16, Bu24, and Bu32), and an alcohol mixture comprised of 10% ethanol and 8% iso-butanol (E10/Bu8). The two 2012 MY vehicles tested over the FTP cycle on a light-duty chassis dynamometer were equipped with stoichiometric, wall-guided SI DI engines with TWCs.

The main findings of this study are that THC and NMHC emissions appeared to be higher for E15 and E20 relative to E10, whereas some reductions in THC and NMHC emissions were seen for the higher butanol blends relative to Bu16. CO emissions were found in relatively low levels for both vehicles, with the Chevrolet Impala emitting higher CO emissions than the Kia Optima. No strong trends were seen between the test fuels for CO emissions. Similar to CO emissions, NO_x emissions did not show any significant trends between the fuels tested, with the Chevrolet Impala showing higher NO_x emission levels compared to Kia Optima. Some reductions were seen in CO_2 emissions for the higher ethanol blends and butanol blends compared to E10 and Bu16, respectively. For CO_2 emissions, the fuel trends weren't consistent with some differences being statistically significant while others were not. Fuel economy, calculated based on the carbon balance method, was systematically lower with increasing ethanol and butanol blend ratios. The lower fuel economy was a result of the lower energy content of the higher ethanol and butanol blends compared to E10 and Bu16, respectively.

PM mass emissions exhibited decreases as the oxygen content in the fuel increased. In most cases the reductions in PM mass emissions for both vehicles were statistically significant. Particle number emissions corroborated the PM mass trends and showed decreases with the higher ethanol and butanol blends relative to E10 and Bu16 respectively.

Black carbon emissions showed statistically significant decreases with E15, E20, and Bu16 relative to E10 for the Chevrolet Impala, while for the Kia Optima most fuels exhibited insignificant differences.

Formaldehyde and acetaldehyde were the predominant carbonyls in the exhaust for both vehicles followed by butyraldehyde, benzaldehyde, crotonaldehyde, methacrolein, and propionaldehyde. Formaldehyde and acetaldehyde showed both increases and decreases with the higher ethanol and butanol blends relative to E10 and Bu16. It was also found that the use of butanol blends enhanced the formation of butyraldehyde emissions. Emissions of 1,3-butadiene did not follow a global trend between the test fuels for both vehicles, showing statistically significant increases for the higher ethanol blends relative to E10 for the Kia Optima and some increases for the higher butanol blends relative to Bu16 for the Chevrolet Impala. Benzene emissions showed elevated emissions for the higher ethanol blends, while some reductions in benzene emissions were observed for the higher butanol blends. For the Kia Optima, E15 and E20 blends led to higher ethylbenzene, toluene, and xylenes emission compared to E10, while the butanol blends exhibited decreases or marginal differences relative to Bu16. For the Chevrolet Impala, the higher ethanol resulted in minimal differences in ethylbenzene, toluene, and xylenes emission compared to E10, while the higher butanol blends trended lower relative to Bu16.

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APPENDIX

Table A1. Main Physicochemical properties of the alcohol fuels

Property	E10	E15	E20	B16	B24	B32	Test Method
Distillation- IBF (°F)	113	110	112	107	98	111	ASTM D86
10 (°F)	137	144	143	148	145	142	
50 (°F)	206	215	163	203	209	207	
90 (°F)	313	309	291	313	317	232	
EP (°F)	344	350	356	341	379	339	
Gravity (°API)	57.8	57.8	57.6	56.3	56.7	55.9	ASTM D4052
Reid Vapor Pressure (psi)	7.0	6.91	7.2	7.1	6.9	7.1	ASTM D5191
Ethanol/ Iso- Butanol Content (vol %)	9.96	15.08	20.10	15.79	24.01	31.86	ASTM D4815
Total Oxygen (wt %)	3.67	5.56	7.41	3.58	5.55	7.35	ASTM D4815
Carbon (wt fraction)	82.54	80.70	78.89	82.79	80.95	79.09	ASTM D5291
Hydrogen (wt fraction)	13.85	13.96	13.70	13.65	13.66	13.56	ASTM D5291
Sulfur (ppm wt)	10	9	7.56	9	8	7	ASTM D5353
Aromatics (vol %)	21.8	19.4	19.4	22.8	20.4	17.8	ASTM D5580
Olefins (vol %)	5.1	4.5	4.5	5.6	5.1	3.6	ASTM D6550
RON	92.9	94.6	94.5	93.0	96.9	97.0	ASTM D2699
MON	84.7	86.1	85.0	84.0	86.2	86.6	ASTM D2700
Octane ((RON+ MON)/2)	88.8	90.4	89.8	88.5	91.6	91.8	ASTM D2699/2700
Net Heat of Combustion (BTU/lb)	18056	17515	17029	17637	17648	17.339	ASTM D240

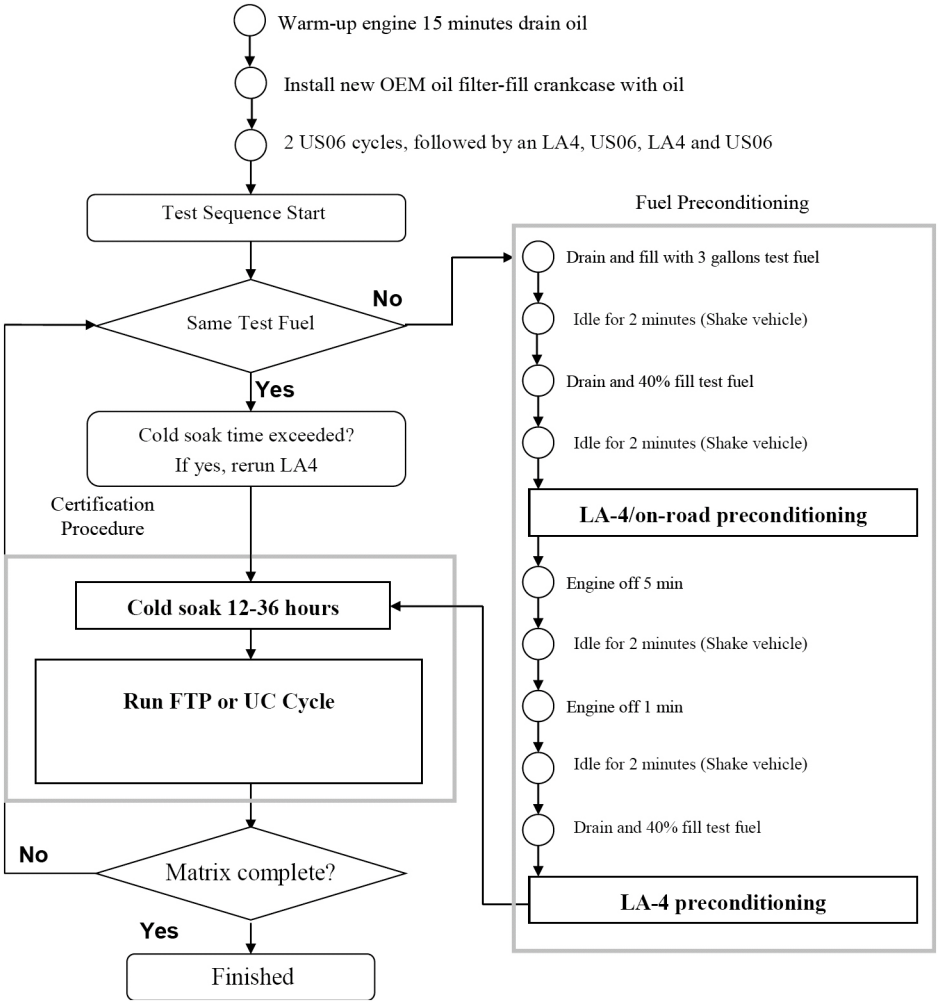

Figure A1. Fuel preconditioning procedure and oil change protocol followed during this study