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Full Length Article

Application of low-level biodiesel blends on heavy-duty (diesel) engines: Feedstock implications on NO_x and particulate emissions

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HIGHLIGHTS

- Low concentration biodiesel blends reduce PM mass, THC, and CO emissions.
- Comprehensive testing on B5/B10 blends shows NO_x emissions increases.
- Methyl ester unsaturation adversely affected NO_x emissions.
- Higher PM with longer chain and more unsaturated methyl esters.

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ABSTRACT

The use of low levels of biodiesel in diesel fuel is becoming more widespread throughout the world, and yet there is still limited information on the actual impact of low concentration biodiesel blends on NO_x emissions. For this purpose, two different methyl ester feedstocks produced from soybean oil and animal tallow were tested at B5 and B10 levels in a 2006 Cummins ISM engine and a 1991 DDC Series 60 engine over the Federal Test Procedure (FTP), the Urban Dynamometer Driving Schedule (UDDS), and the Supplementary Emission Test (SET) cycles. Increases in nitrogen oxide (NO_x) emissions were found for the unsaturated soy B5/B10 blends for the 2006 Cummins engine over the FTP and UDDS cycles and for the 1991 DDC engine over different combinations of all three cycles. Unlike the unsaturated soy blends, the higher saturated animal fat-based biodiesel did not show consistent NO_x increases, with only the B10-animal blend showing a statistical significant increase for the FTP on the 1991 DDC engine. The differences in NO_x emissions between the biodiesel feedstocks were likely due to differences in the degree of unsaturation in the ester. The low level biodiesel blends also showed reductions in particulate matter (PM), total hydrocarbon (THC), and carbon monoxide (CO) emissions, consistent with the trends seen for higher biodiesel blend levels.

1. Introduction

In an effort to reduce greenhouse gas (GHG) emissions and fossil-based fuel consumption, biofuels have attracted attention as alternatives to conventional fuels in the transportation sector. In the US, biofuels have been promoted by several legislative measures, including the Energy Independence and Security Act (EISA 2007) and the Renewable Fuel Standard (RFS), which was initiated in 2005 and expanded in 2007 [1,2]. The latter mandates the use of 36 billion gallons of renewable fuels in the transportation fuel pool by 2022. Although this target is expected to be met primarily with ethanol, biodiesel is steadily developing in the US market. Unlike most European Union countries where biodiesel is the biofuel of choice in the transportation sector, in the US biodiesel fuel volumes are considerably less than those of ethanol due to the dominance of gasoline vehicles. However, the recently released proposed rule by the US Environmental Protection Agency (USEPA) for the 2014–2017 RFS requires a significant growth for biodiesel volumes ranging from 1.63 to 1.90 billion gallons per year [3].

Fatty acid methyl esters (FAMEs), commonly known as biodiesel, can be derived from any vegetable oil (edible and non-edible), waste cooking oil, or animal fat [4]. Biodiesel is produced via the transesterification reaction, also called alcoholysis, of oils (triglycerides) with alcohol in the presence of an alkaline or an acidic catalyst [5]. During the past decade, biodiesel has been

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extensively investigated in test cell engines, light-duty vehicles, and heavy-duty vehicles [6–9]. Many studies have generally reported a decrease in total hydrocarbon (THC), carbon monoxide (CO), and particulate matter (PM) emissions with either neat or blended biodiesel compared to petroleum diesel fuel [10,11]. For PM emissions, the majority of studies have largely shown strong reductions when biodiesel is used as a consequence of the oxygen content and the absence of aromatic and sulfur compounds in the fuel [12,13]. Previous investigations have also shown a biodiesel feedstock dependence on PM emissions [14,15]. Lapuerta et al. [16] have shown in their experiments that more unsaturated biodiesels decreased PM emissions by 20%. On the other hand, Salamanca et al. [17] showed that more unsaturated as opposed to more saturated methyl esters compounds in the fuel favored the soot precursor's formation in the combustion zone and thus PM emissions. Similarly, in a more fundamental study, Sarathy et al. [18] found that more unsaturated methyl esters have a greater tendency to soot formation than more saturated esters.

For nitrogen oxide (NO_x) emissions, on the other hand, biodiesel shows a tendency to increase emissions according to the majority of the published literature. Several studies have shown that NO_x emissions may be sensitive to biodiesel source material and properties [7,16,19,20]. McCormick et al. [21] showed strong correlations between NO_x, fuel density and cetane number, and interrelations among the number of double bonds and the chain length of biodiesel. Schönborn et al. [22] also reported that molecules with longer fatty acid chain lengths produced less NO_x during combustion than shorter length molecules. Szybist et al. [23] investigated the effect of biodiesel on NO_x formation and reported an advance of the start of injection with increasing biodiesel content. They attributed this phenomenon to the increased bulk modulus of biodiesel relative to diesel fuel, which has a greater impact in older engines with pump-line-nozzle and unit injector fuel systems as opposed to modern high pressure common-rail systems. More comprehensive investigations concluded that the origin of the biodiesel NO_x increase is based on having reacting mixtures that are closer to stoichiometric during the ignition and in the autoignition zone [24].

While studies have generally shown NO_x increases for higher level biodiesel blends, the impact of biodiesel on NO_x emissions at levels of B20 and below has still been a source of controversy [8,21,25]. Studies of NO_x emissions impacts for blends below B20 have been relatively limited, and few studies have included sufficient replicates to adequately characterize the potential small NO_x impacts that might be seen at such low levels. Although the NO_x increases at levels less than B20 would be expected to be small, as low level biodiesel continues to expand in the marketplace, such increases need to be better quantified to better understand any potential air quality impacts from biodiesel use. Emissions of NO_x are contributing to ground-level ozone, which is the primary ingredient of photochemical smog, and can also contribute to secondary PM formation [26]. This could be an important consideration in Europe, for example, where diesel vehicles represent a substantial portion of the fleet, and where biodiesel is utilized at B7 level. Low levels of biodiesel are also becoming more prevalent in the US, and in California with the introduction of the Low Carbon Fuel Standard (LCFS).

The potential for NO_x emissions increases for biodiesel fuels was long been recognized by the California Air Resources Board (CARB) and remains an issue for the widespread penetration of biodiesel in the State of California. Over the years, the revolutionary changes required for diesel engines have provided significant reductions in NO_x emissions with the use of exhaust aftertreatment controls, such as selective catalytic reduction (SCR). In California, where a number of urban areas do not meet the national ambient air quality standards (NAAQS), in addition to the NO_x emissions reductions from heavy-duty diesel vehicles, the fuel formulations are also being controlled in order to protect urban air quality. Therefore, the use of biodiesel as an automotive fuel in California represents a more complex issue as it involves maintaining NO_x neutrality, low blend concentrations, and understanding the differences in specific raw materials that can be used in producing biodiesel. While the NO_x impacts of low level biodiesel blends may not be as important from a regulatory perspective outside of California, it is still important to better quantify the emissions impacts of low level biodiesel throughout the world.

The purpose of this study is to investigate the gaseous and PM emissions impacts from lower biodiesel blends in two heavy-duty diesel engines using a robust procedure that is similar to that used for certifying diesel fuels in California under the emissions equivalent diesel certification procedure. This work provided important information that was utilized to understand the potential impacts of widespread low level biodiesel use in California, and represented an important part of the scientific information that was utilized in the development of CARB's Alternative Diesel Fuel (ADF) Regulation and LCFS. For this study, emission measurements were performed on 5% and 10% biodiesel blends by volume prepared from soybean oil methyl ester and animal fat methyl ester. Testing was conducted on a 2006 Cummins ISM engine and a 1991 Detroit Diesel Corporation (DDC) Series 60 engine over the standard Federal Test Procedure (FTP), the Urban Dynamometer Driving Schedule (UDDS), and the Supplemental Emissions Test (SET). The results of this work are discussed in the context of different biodiesel feedstocks and the influence of operating conditions.

2. Experimental

2.1. Test fuels

A total of five fuels were employed in this study. The baseline fuel was a typical on-road CARB ultra-low sulfur diesel (ULSD). Two methyl esters produced from soybean oil (SME) and animal fat oil (AFME) were obtained from BQ-9000 suppliers and were used as blendstocks with the CARB ULSD to create biodiesel blends of 5 vol% (B5) and 10 vol% (B10), respectively. The two biodiesels selected represent some of the more widely used feedstocks in the US and also span a relatively wide range of biodiesel properties that might be found in the marketplace in terms of cetane number and degree of unsaturation. The neat methyl esters were tested for fuel properties according to ASTM D6751, while the CARB ULSD and the B5/B10 blends were tested for fuel properties according to ASTM D675. The major physicochemical properties of the test fuels are given in Table 1, while the properties of the neat methyl esters are provided in the Supplementary Material. Some of the key properties for the neat biodiesels in terms of their emissions characteristics include the cetane number (58 for the animal-based biodiesel vs. 47 for the soy-based biodiesel), C/H ratio (0.517 for the animal-based biodiesel vs. 0.544 for the soy-based biodiesel), which is an indication of the degree of saturation of the biodiesel, and density (0.875 for the animal-based biodiesel vs. 0.885 for the soy-based biodiesel).

2.2. Test engines, cycles, and test sequence

Two engines were used for this study, including a 2006 model year Cummins ISM 370 engine with a common rail fuel injection system, a turbocharger, and exhaust gas recirculation (EGR) and a 1991 model year Detroit Diesel Corporation (DDC) Series 60 engine. The 2006 Cummins ISM represents the last generation of diesel engine technology that did not require aftertreatment. The 1991 DDC Series 60 engine is the engine that has traditionally been

Table 1
Fuel properties of CARB ULSD and the biodiesel blends.

Property	ASTM test method	Units	CARB ULSD	B5 animal	B5 soy	B10 animal	B10 soy
API gravity at 60 °F	ASTM D4052	API	38.8	38.2	38.3	38.0	37.8
Density at 15 °C	ASTM D4052	g/ml	0.8306	0.8333	0.8332	0.8346	0.8355
Cetane number	ASTM D613		53.4	56.3	52.9	57.1	53.4
Heating value	ASTM D240	BTU/lb	19,773	19,590	19,609	19,480	19,509
Carbon unit per energy		Carbon lbs./BTU	4.36×10^{-5}	4.36×10^{-5}	4.33×10^{-5}	4.37×10^{-5}	4.37×10^{-5}
Biodiesel content	ASTM D7371		–	5.3	5.2	9.9	9.8
Carbon	ASTM D5291	wt%	86.17	85.44	84.87	85.04	85.17
Hydrogen	ASTM D5291	wt%	13.63	13.56	13.53	13.5	13.49
Oxygen	D5291 (by difference)	wt%	–	1.0	1.6	1.46	1.34
Flash point	ASTM D93	°C	163	76	76	75	73
Water and sediment	ASTM D2709	vol%	<0.02	<0.02	<0.02	<0.02	<0.02
Kinematic viscosity at 40 °C	ASTM D445	mm^2/s	3.069	3.131	3.105	3.178	3.147
Total aromatics	ASTM D5186	vol%	22.6				
Sulfur	ASTM D5453	ppm	7.8	7.5	7.6	7.9	6.5
Copper strip corrosion	ASTM D130		1A	1A	1A	1A	1A
Lubricity	ASTM D6079	μm	–	201	319	214	183
Pour point	ASTM D97	°C	−6	−6	−6	−6	−6
Ramsbottom carb. res.	ASTM D524	mass%	0.06	0.04	0.06	0.06	0.04

used for the emissions equivalent diesel certification procedure in California. The main engine specifications are provided in the Supplementary Material.

Emissions testing were conducted over the Federal Test Procedure (FTP), the Urban Dynamometer Driving Schedule (UDDS), and the Supplemental Emissions Test (SET). The SET cycle is a 13-mode, steady-state engine dynamometer test cycle for heavy-duty engines. The test sequence for the FTP and the UDDS emissions testing was conducted using one of the hot start sequences described under title 13, California Code of Regulations (CCR), section 2282(g)(4)(c) 1.b Alternative 1. The test sequence for the FTP and UDDS cycles is shown in the Supplementary Material. This sequence was repeated over two days to provide a total of 8 replicates on both the baseline CARB ULSD and the biodiesel blend. Since the SET cycle is longer than the FTP, fewer tests were conducted each day. A total of 4 tests were run for each day of SET testing, as shown in the Supplementary Material. Although fewer replicates were conducted on the SET cycle, this cycle contains 13 different steady-state segments, which provides additional levels of replication for statistical comparisons. This sequence was repeated over two days to provide a total of 4 replicates on both the baseline CARB ULSD and the biodiesel blend.

2.3. Emissions testing

All tests were conducted in CE-CERT's heavy-duty engine dynamometer laboratory. This laboratory is equipped with a 600-hp General Electric DC electric engine dynamometer. Emissions measurements were obtained using the CE-CERT Mobile Emissions Laboratory (MEL). The facility and sampling setup have been described in detail previously and are only discussed briefly here [27]. For all tests, standard emissions measurements of THC, non-methane hydrocarbons (NMHC), methane (CH_4), CO, NO_x, carbon dioxide (CO_2), and PM, were measured. CO and CO_2 emissions were measured with a 602P nondispersive infrared (NDIR) analyzer from California Analytical Instruments (CAI). THC, NMHC, and CH_4 emissions were measured with a 600HFID flame ionization detector (FID) from CAI. NO_x emissions were measured with a 600HPLC chemiluminescence analyzer from CAI. The mass concentrations of PM were obtained by analysis of particulates collected on 47 mm diameter 2 μm pore Teflo filters (Whatman brand). The filters were measured for net gains using a UMX2 ultra precision microbalance with buoyancy correction following the weighing procedure guidelines of the Code of Federal Regulations (CFR). Fuel consumption was determined from these emissions measurements via carbon balance using the densities and carbon weight fractions from the fuel analysis.

Carbonyl compounds and elemental and organic carbon (EC/OC) fractions were also measured for a subset of triplicate samples collected during FTP testing for each fuel combination. Samples for carbonyl analysis were collected onto 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA). A critical flow orifice controlled the flow to 1.0 L/min through the cartridge. 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 (200 cm × 4.6 mm ID) with an upstream guard column. The HPLC sample injection and operating conditions were set up according to the specifications of the SAE 930142HP protocol. Samples from the dilution air were collected for background correction. EC/OC samples were collected simultaneously on pre-cleaned QAT Tissuquartz quartz-fiber filters (Pall-Gelman, Ann Arbor, MI, USA). Quartz fiber filters were pre-cleaned to remove carbonaceous contaminants by firing for 4 h at 600 °C. A Thermal/Optical Carbon Aerosol Analyzer (Sunset Laboratory, Forest Grove, OR) operating using the NIOSH (National Institute of Occupational Safety and Health) Method 5040 was used to analyze OC and EC.

The results shown in the following figures/tables represent the average of all test runs performed on that fuel for the specific engine and cycle. The error bars represent one standard deviation on the average value. Statistical analyses were performed using a 2-tailed, 2-sample, equal-variance *t*-test. Each B5/B10 biodiesel blend was compared against the CARB ULSD tests conducted over the two-day test sequence on that particular B5 or B10 blend. The CARB ULSD values for the individual comparisons are denoted in the figures as "CARB vs. Blend Name". The statistical analyses provide information on the statistical significance of the different individual findings. This following discussion focuses predominantly on results that were found to be either statistically significant or marginally statistically significant. Results are considered to be statistically significant for p values $\leqslant 0.05$. Results are considered marginally statistically significant for $0.05 \leqslant p < 0.1$.

3. Results and discussion

3.1. NO_x emissions

Emissions of NO_x, expressed on a gram per brake horsepower hour (g/bhp-h) basis, for the different B5 and B10 blends for the

Cummins ISM and DDC Series 60 engines are shown in Fig. 1. More detailed information on the average values, percentages differences, and statistical results for the NO_x emissions are also included in the Supplementary Material (Table S5). Overall, NO_x emissions for the testing for the Cummins ISM engines showed statistically significant increases of 1.0% and 1.9%, respectively, for the B5 and B10 soy blends compared to CARB ULSD for the FTP cycle. For the UDDS cycle for this engine, only the B10-soy blend showed a statistically significant increase of 3.6% compared to CARB ULSD. Although B5-soy produced higher NO_x emissions relative to CARB ULSD over the UDDS cycle, these differences where not statistically significant. For the B5/B10 animal fat blends for the Cummins ISM engine, NO_x emissions trended lower compared to CARB ULSD, however, none of the differences seen were statistically significant.

Similar to the Cummins engine, the more unsaturated blends showed systematic NO_x increases for the DDC Series 60 engine, with the B5-soy blend showing a statistically significant increase of 1.0% and 3.2%, respectively, for the FTP and UDDS cycles. The B10-soy blend showed statistically significant increases of 1.5% and 1.3%, respectively, for the FTP and SET cycles. For this engine, the B10-animal blend produced a statistically significant increase of 0.8% compared to CARB ULSD for the FTP, but not for the other test cycles. The B5-animal blend did not show any statistically significant differences in NO_x emissions for any of the three tests cycles.

Both engines showed some statistically significant differences in NO_x emissions for the individual modes of the SET cycle, as shown in Table S6 (Supplementary Material). Although the overall SET emissions differences were statistically significant only for the B10-soy blend for the 1991 DDC Series 60 engine, statistically significant NO_x increases for the B5-soy and B10-soy blends ranged from 1.6% to 4.4%, respectively, were also observed for the 2006 Cummins ISM engine. B10-animal showed a 3.1% marginally statistically significant reduction in NO_x emissions for the 2006 Cummins ISM engine for mode 1, which is the idle mode. For the 1991 DDC Series 60 engine, statistically significant and marginally statistically significant increases for the biodiesel blends ranged from 1.0% to 2.9% for different modes.

The results reported here are in agreement with previous studies showing higher NO_x emissions with biodiesel use [6,7,28,29]. The increase in NO_x emissions with biodiesel is likely attributed to the oxygen content in the biodiesel and the increased stoichiometric burning (less rich) for biodiesel blends, which led to higher combustion temperatures and NO_x emissions [24]. However, the causes of differences in NO_x emissions between the biodiesel blends and the baseline diesel could be attributed to fuel physicochemical compositional factors, such as the different degrees of unsaturation present in the two biodiesels. The trend of greater NO_x increases for more unsaturated biodiesel blends has been seen in a number of previous studies [8,12,21]. The larger increases in NO_x emissions for the more unsaturated soy-based blends could be a consequence of several contributing factors. Fuels with a higher degree of unsaturation, and a correspondingly higher C/H ratio, tend to have higher adiabatic flame temperatures, which would lead to higher NO_x emissions [6,30]. In addition, the cetane number, which intercorrelates with the degree of unsaturation, could have played a key role in determining NO_x emissions for the soy-based blends [21,30]. Lower cetane number lengthens the ignition delay, leading to more premixed burning and higher in-cylinder gas averaged temperatures during the combustion event, and subsequently favoring the formation of thermal NO_x [30,31]. Higher rates of CH radical generation favoring the formation of prompt NO_x and the longer ignition delay favoring the formation of NO_x due to the longer residence time of the combustion products at higher temperatures could also contribute to higher NO_x emissions for the soy-based biodiesel blends [31,32].

3.2. PM emissions

Fig. 2 shows the PM mass emissions results of the different B5 and B10 blends for the 2006 Cummins ISM and 1991 DDC Series 60 engines. More detailed information on the average values, percentages differences, and statistical results for the PM mass emissions are also included in the Supplementary Material (Table S7). For the 2006 Cummins ISM engine, PM emissions showed consistent, statistically significant reductions ranging from 5.8% to 15.1% with all B5 and B10 blends tested over the FTP cycle. Statistically significant reductions in PM emissions ranging from 6.7% to 14.3% were seen for the biodiesel blends over the SET cycle. There were some inconsistencies in the PM emissions for the UDDS cycle, with a marginally statistically significant increase of 6.4% for the B5-soy compared to CARB ULSD for the 2006 Cummins ISM engine. This might be due to the low load profile of this cycle.

The same trend was seen for the 1991 DDC Series 60 engine with the statistically significant reductions ranging from 7.5% to 16.5% for the B5 and B10 blends over the FTP cycle. All the biodiesel blends showed either statistically significant or marginally statistically significant reductions in PM emissions for the SET cycle, which ranged from 6.0% to 9.4% compared to CARB ULSD. Like the newer engine, PM results for the 1991 DDC Series 60 engine

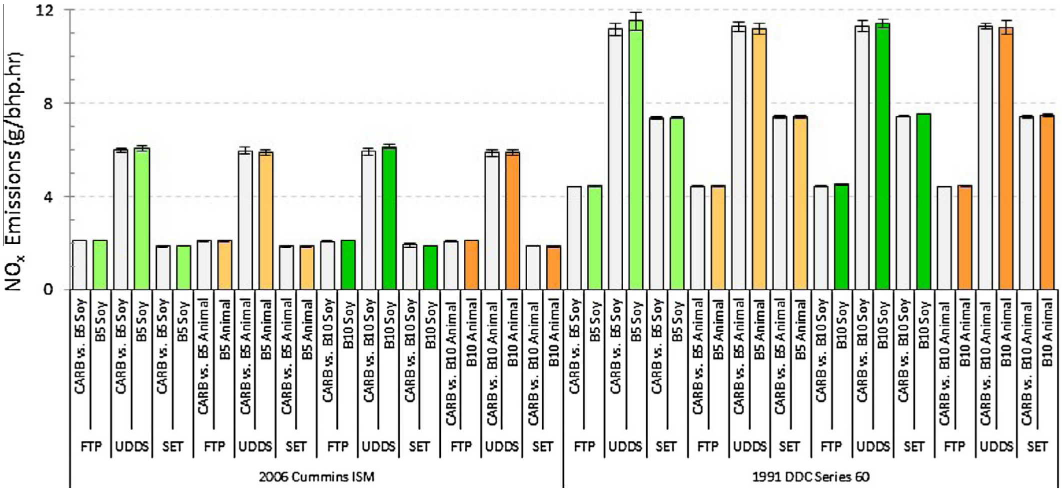

Fig. 1. Average NO_x emission results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP, UDDS, and SET cycles.

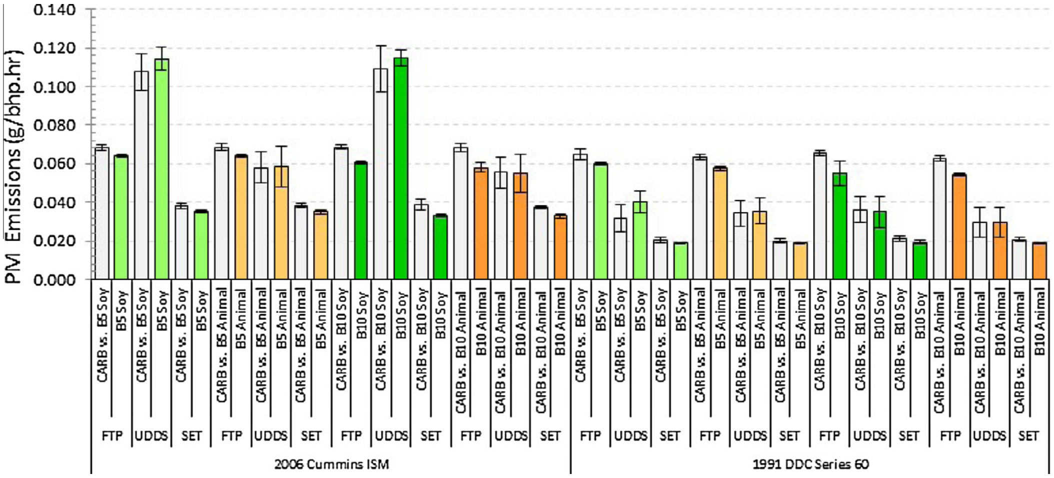

Fig. 2. Average PM emission results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP, UDDS, and SET cycles.

showed some inconsistences for the UDDS cycle. None of the differences seen in PM emissions for the 1991 DDC Series 60 engine for the UDDS were statistically significant, except for the B5-soy biodiesel which showed a 26.6% increase compared to CARB ULSD.

The lower PM emission results with the biodiesel blends are in accordance with previous studies, and there is a consensus among authors that the fuel-borne oxygen and the lack of aromatics lead to a cleaner combustion and generally explain the PM reductions [10,16,31,33]. Looking at the average values for the soy biodiesel blends vs. the animal biodiesel, the more unsaturated biodiesel blends showed slightly higher PM emissions compared to the more saturated blends (as shown in the Supplementary Material, Table S7). However, the corresponding CARB tests conducted in conjunction with the soy- and animal-based biodiesel blend testing also showed similar slight increases for the soy-based compared to the animal-based blend testing. So, the overall percentage reductions with respect to the CARB ULSD are similar between the soy- and animal-based blends, except for a few tests conducted over the UDDS cycles. Previous studies in our laboratory at higher soy- and animal-based blend levels also did not show consistent differences with respect to PM mass emissions and saturation level [34]. Other studies have shown a tendency for more unsaturated biodiesels having a greater propensity to form soot precursors than more saturated biodiesel fuels, such as acetylene (C_2H_2) which is intermediate to soot precursor formation [18,22,35,36]. Some studies have also shown PM emissions were influenced by the chain length of the methyl ester, a characteristic that correlates with the degree of saturation, with shorter methyl ester chain lengths usually associated with higher oxygen content by weight, which is the primary driver for reducing soot formation, enabling a more complete combustion even in fuel-rich regions of the combustion chamber [37].

3.3. THC and CO emissions

The THC emissions for the different B5 and B10 blends on both engines is shown in Fig. 3. Although THC emissions showed a general decreasing trend for most biodiesel blends over most of the test cycles compared to CARB ULSD, these differences were only statistically significant or marginally statistically significant for the B5-soy blend for the SET cycle for the 2006 Cummins ISM engine and the B5-animal and B10-animal blends for the SET cycle and the B10-soy blend for the FTP for the 1991 DDC Series 60 engine. THC emissions produced some statistically and marginally statistically significant reductions for the biodiesel blends compared to CARB ULSD over the different modes of SET cycle, ranging from 0.1% to 28.4% over the two engines and the range of blends tested, as shown in Table S8 (Supplementary Material). The higher oxygen concentration of biodiesel is one of the main factors contributing to lower THC emissions, which leads to a more complete combustion and leaner burn during the diffusion combustion phase [15,31].

CO emissions are presented in Fig. 4. CO emissions results showed a general trend of reductions with the biodiesel blends, although these differences were not statistically significant for all biodiesel blends or cycles. The statistically significant and marginally statistically significant reductions ranged from 2.0% to 7.9% for the 2006 Cummins ISM engine and 2.3% to 7.3% for the 1991 DDC engine for the different biodiesel blends and cycles. There was a somewhat stronger trend of biodiesel CO reductions for the 1991 DDC engine, which showed CO reductions for nearly all biodiesel blends and cycles with the exception of some UDDS cycles, compared to the 2006 Cummins engine. Reductions were also seen for individual modes of the SET cycle for both engines, with most of the statistically significant reductions being on the order of 12% or less, as shown in Table S9 (Supplementary Material). The lower CO emissions with biodiesel blends were primarily due to the oxygen content in the fuel that favors more complete combustion [33].

3.4. CO_2 emissions and brake specific fuel consumption

The CO_2 emission results for the biodiesel blends are shown in Fig. 5. CO_2 emissions did not show consistent fuel trends over the range of blends, cycles, and engines tested, with nearly all differences not being statistically significant. Other studies have shown increases in exhaust CO_2 emissions with biodiesel, which could be related to the generally higher carbon content per unit of energy for biodiesel compared to typical diesel fuel [21,38]. For the present study, the differences in the carbon content per unit energy between the CARB ULSD are very minor, however, due to the relatively low blend levels.

The brake specific fuel consumption (BSFC) resulted in some increasing trends with the biodiesel blends, although this was not seen for all biodiesel blends, cycles, and engine combinations (Fig. 6). For the 2006 Cummins engine, these BSFC increases ranged from 0.5% to 2.3%. For the 1991 DDC engine, these BSFC increases ranged from 0.7% to 3.2%. These results are directionally consistent with the results of previous studies [7,10,21,38]. The increases in

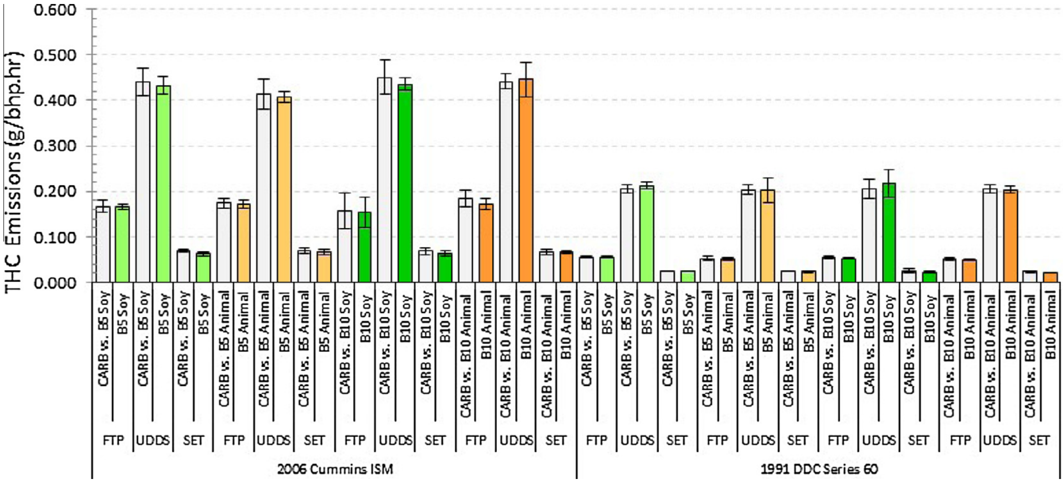

Fig. 3. Average THC emission results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP, UDDS, and SET cycles.

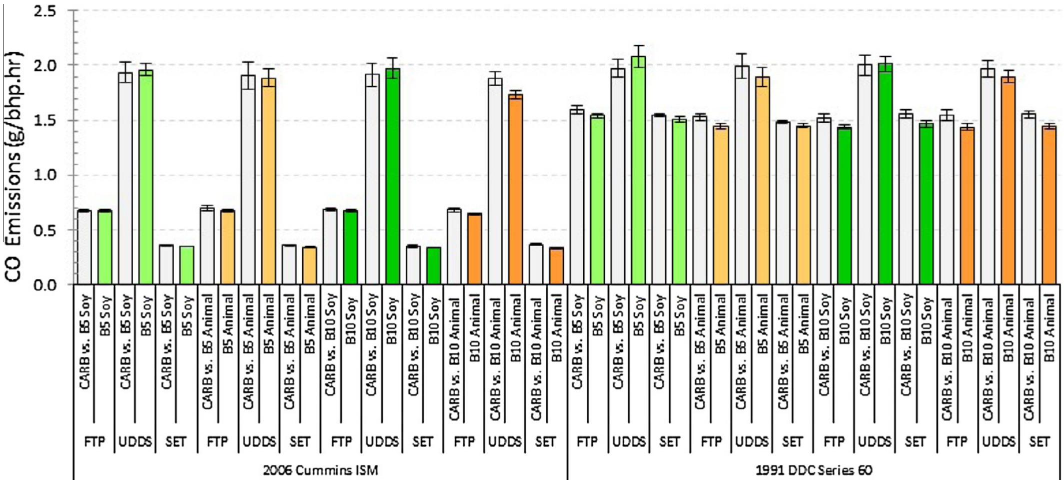

Fig. 4. Average CO emission results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP, UDDS, and SET cycles.

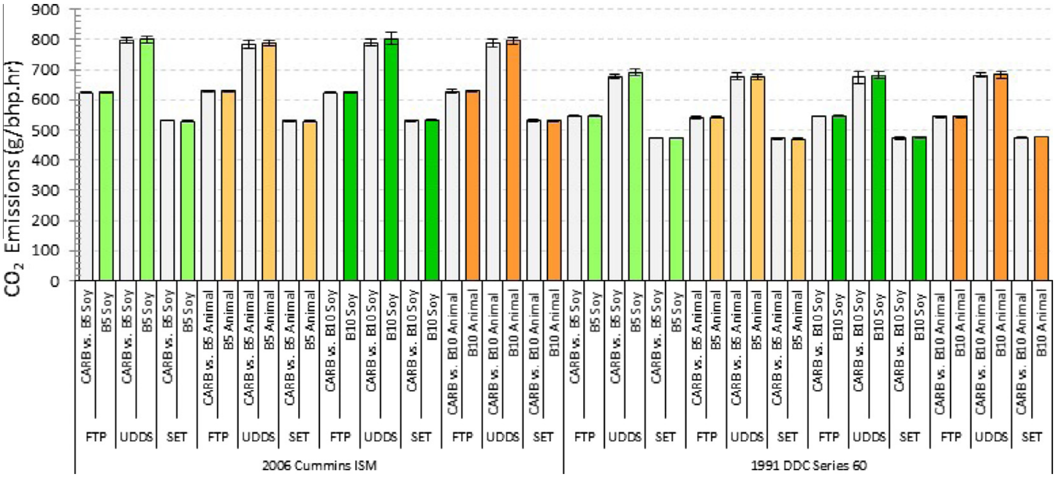

Fig. 5. Average CO_2 emission results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP, UDDS, and SET cycles.

BSFC were comparable to the difference in the energy content between the CARB ULSD and B5 and B10 blends, as shown in the Supplementary Material, which are on the order of 0.9% for the B5 blends and 1.4% for the B10 blends.

3.5. EC/OC emissions

Elemental and organic carbon (EC/OC) fractions are shown in Fig. 7. EC/OC emissions were only analyzed over the FTP cycle for

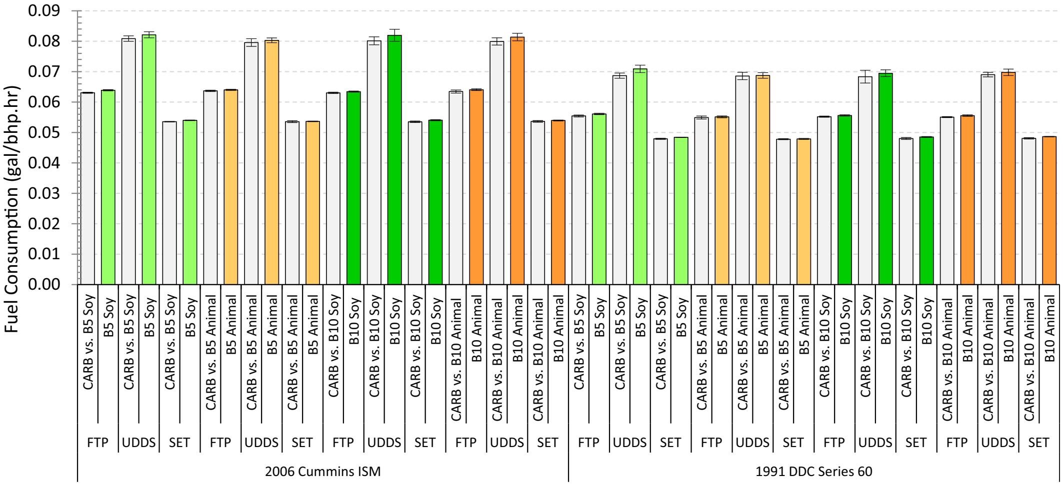

Fig. 6. Average brake specific fuel consumption results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP, UDDS, and SET cycles.

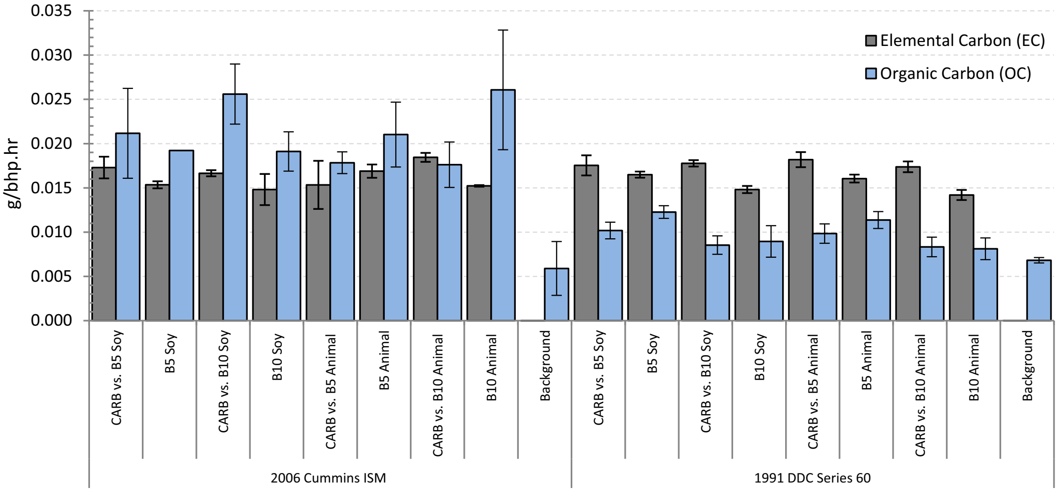

Fig. 7. Average EC/OC emission results for B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP cycle.

both test engines. Overall, the results for the EC/OC emissions were not as consistent as those for the total PM mass. For the 2006 Cummins ISM engine, PM was dominated by OC, whereas for the 1991 DDC Series 60 engine the PM emissions were clearly dominated by EC. Statistically significant reductions in EC were seen for the B5 animal, B10 soy and B10 animal blends for the 1991 DDC Series 60 engine, but only for the B10 animal blend for the 2006 Cummins engine. For OC emissions, the only statistically significant difference found was a 20.5% increase for the B5 soy blend for the 1991 DDC Series 60 engine. The EC/OC results reported here were engine-specific, since the older1991 DDC Series 60 engine showed higher EC emissions than the 2006 Cummins ISM engine. Generally, higher combustion temperature and more local fuel-rich regions can produce more EC emissions [39]. The 1991 DDC Series 60 engine has less advanced controls of the combustion which likely leads to more local fuel-rich zones and hence more EC emissions. For the 1991 DDC Series 60 engine, it is also possible that higher combustion temperatures in the cylinder contributed in more EC emissions in line with the higher NO_x emissions. OC is generally formed from the incomplete combustion of fuel and lubricant oil [40]. For the 2006 Cummins ISM engine, the higher OC emissions could be explained by the fact that the low load conditions experienced over the FTP resulted in low combustion temperatures, which inhibited the pyrolysis of the fuel and lubricant oil [40].

3.6. Carbonyl emissions

The carbonyl emissions, expressed on a mg/bhp-h basis, for the B5 and B10 blends for both test engines are shown in Table 2. Carbonyl emissions were only measured over the FTP cycle. Consistent with previous studies, low molecular-weight aldehydes, such as formaldehyde and acetaldehyde, were predominant in the exhaust [11,37,41]. Heavier aldehydes were also present, but in lesser amounts. Although there was a weak trend showing lower formaldehyde and acetaldehyde emissions with the use of biodiesel blends, statistical analysis did not show consistent fuel differences between the CARB ULSD and the biodiesel blends. Reductions in carbonyl emissions with biodiesel have been observed by others [42,43]. These reductions are usually ascribed to the decomposition of esters via decarboxylation, which can decrease the probability of forming oxygenated combustion intermediates with respect to conventional diesel combustion [33].

Table 2

Carbonyl emissions for the B5 and B10 biodiesel blends when tested on the 2006 Cummins ISM and 1991 DDC Series engines for FTP cycle.

			Formaldehyde	Acetaldehyde	Acrolein	Propionaldehyde	Crotonaldehyde	Methacrolein	MEK	Butyraldehyde	Benzaldehyde	Valeraldehyde
2006 Cummins ISM	Average ± std dev (mg/bhp-h)	CARB vs. B5 soy	16.71 ± 2.308	7.521 ± 0.198	−0.116 ± 0.125	1.181 ± 0.103	0.436 ± 0.079	0.467 ± 0.00	0.304 ± 0.03	1.164 ± 0.910	0.177 ± 0.006	1.103 ± 0.285
		B5 soy	16.68 ± 0.975	7.852 ± 0.786	−0.204 ± 0.001	1.454 ± 0.102	0.556 ± 0.048	0.638 ± 0.09	0.000 ± 0.00	2.421 ± 0.220	−0.163 ± 0.00	1.369 ± 0.498
		CARB vs. B10 soy	15.68 ± 0.269	4.125 ± 0.119	−0.080 ± 0.056	0.666 ± 0.023	0.229 ± 0.012	0.272 ± 0.06	0.000 ± 0.00	1.230 ± 0.004	0.041 ± 0.023	0.062 ± 0.013
		B10 soy	14.87 ± 1.061	3.901 ± 0.217	−0.106 ± 0.005	0.703 ± 0.060	0.206 ± 0.013	0.259 ± 0.06	0.099 ± 0.00	1.286 ± 0.012	0.052 ± 0.052	0.401 ± 0.463
		CARB vs. B5 animal	18.33 ± 1.554	4.418 ± 0.314	−0.117 ± 0.123	0.798 ± 0.096	0.284 ± 0.015	0.394 ± 0.02	0.138 ± 0.03	0.208 ± 0.088	0.174 ± 0.212	0.512 ± 0.515
		B5 animal	16.81 ± 0.998	4.214 ± 0.198	−0.098 ± 0.014	0.725 ± 0.022	0.275 ± 0.028	0.150 ± 0.32	0.130 ± 0.00	0.117 ± 0.042	0.001 ± 0.037	0.436 ± 0.592
		CARB vs. B10 animal	18.28 ± 0.433	4.568 ± 0.146	−0.127 ± 0.110	0.832 ± 0.019	0.475 ± 0.211	0.352 ± 0.10	0.066 ± 0.09	1.021 ± 1.202	−0.072 ± 0.13	0.883 ± 0.051
		B10 animal	17.92 ± 0.452	4.433 ± 0.124	−0.179 ± 0.037	0.770 ± 0.020	0.296 ± 0.001	0.402 ± 0.02	0.116 ± 0.00	0.148 ± 0.019	0.022 ± 0.029	0.095 ± 0.061
1991 DDC Series 60	Average ± std dev (mg/bhp-h)	CARB vs. B5 soy	4.94 ± 0.270	2.122 ± 0.088	0.123 ± 0.028	0.311 ± 0.152	0.173 ± 0.007	0.150 ± 0.01	0.057 ± 0.05	0.295 ± 0.275	−0.007 ± 0.07	0.230 ± 0.231
		B5 soy	5.09 ± 0.224	1.769 ± 0.588	0.123 ± 0.051	0.338 ± 0.148	0.136 ± 0.041	0.102 ± 0.04	0.046 ± 0.04	0.327 ± 0.157	−0.033 ± 0.06	0.079 ± 0.178
		CARB vs. B10 soy	1.93 ± 0.34	0.436 ± 0.10	0.090 ± 0.03	0.066 ± 0.036	0.059 ± 0.003	0.005 ± 0.09	0.000 ± 0.00	0.047 ± 0.12	−0.062 ± 0.04	−0.071 ± 0.02
		B10 soy	1.85 ± 0.17	0.398 ± 0.03	0.103 ± 0.03	0.035 ± 0.009	0.058 ± 0.007	0.020 ± 0.09	0.000 ± 0.00	−0.026 ± 0.00	−0.090 ± 0.00	−0.054 ± 0.10
		CARB vs. B5 animal	1.99 ± 0.08	0.415 ± 0.05	0.054 ± 0.04	0.059 ± 0.013	0.068 ± 0.014	−0.021 ± 0.05	0.000 ± 0.00	−0.026 ± 0.00	−0.090 ± 0.0	−0.003 ± 0.21
		B5 animal	1.76 ± 0.10	0.395 ± 0.03	0.020 ± 0.03	0.037 ± 0.016	0.046 ± 0.005	−0.028 ± 0.03	0.000 ± 0.00	−0.026 ± 0.00	−0.055 ± 0.06	−0.083 ± 0.03
		CARB vs. B10 animal	2.75 ± 1.10	0.591 ± 0.20	0.123 ± 0.04	0.076 ± 0.038	0.053 ± 0.007	0.060 ± 0.00	0.000 ± 0.00	0.078 ± 0.09	−0.045 ± 0.03	0.015 ± 0.11
		B10 animal	1.97 ± 0.09	0.400 ± 0.03	0.137 ± 0.01	0.034 ± 0.005	0.051 ± 0.011	0.053 ± 0.01	0.000 ± 0.00	0.046 ± 0.12	−0.038 ± 0.09	−0.065 ± 0.03

4. Conclusions

This study attempted to fill in a gap of the understanding on the actual impact of low concentration biodiesel blends on NO_x emissions. The main goal of this work was to more comprehensively study the effects of B5/B10 blends from different feedstocks with CARB ULSD on exhaust emissions to better shape and evaluate California's ADF regulation and LCFS. For this purpose, two different methyl ester feedstocks produced from soybean oil and animal tallow were blended with CARB ULSD and tested in a 2006 Cummins ISM engine and a 1991 DDC Series 60 engine over the FTP, the UDDS, and the SET cycles.

The results of this study revealed that NO_x emissions for the 2006 Cummins ISM engine showed increases for the more unsaturated soy B5/B10 blends compared to CARB ULSD for the FTP and UDDS cycles. For the 1991 DDC Series 60 engine, NO_x emissions also showed increases for the B5-soy blend for the FTP and UDDS cycles, while the B10-soy blend showed increases for the FTP and SET cycles. Unlike the more unsaturated soy blends, the more saturated animal biodiesel did not show consistent NO_x increases, with only the B10-animal blend showing a statistical significant increase for the FTP on the 1991 DDC engine. The differences in NO_x emissions between the biodiesel feedstocks were likely due to differences in the degree of unsaturation in the ester.

PM emissions generally showed consistent reductions for the biodiesel blends for both engines for the FTP and SET cycles, with some inconsistencies for the UDDS cycle. The lower PM emissions for the biodiesel blends relative to CARB ULSD were due to the presence of oxygen in the methyl ester. THC and CO emissions showed a general decreasing trend for most biodiesel blends over most of the test cycles compared to CARB ULSD. On the other hand, CO_2 emissions did not show consistent fuel trends over the range of blends, cycles, and engines tested, with most differences not being statistically significant. As expected, BSFC showed increasing trends with the biodiesel blends as a result to the differences in the energy contents of the fuels. Under the present test conditions, EC/OC results were not as consistent as those for PM mass, with the EC/OC results being more engine-specific. Formaldehyde and acetaldehyde were the predominant aldehydes in the exhaust, and the use of biodiesel did not have a significant impact on carbonyl emissions.

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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.2016.05.001.

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