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Impacts of biodiesel feedstock and additives on criteria emissions from a heavy-duty engine

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ABSTRACT

The reduction of emissions from diesel engines has been a key element in obtaining air quality and greenhouse gas reduction goals. Biodiesel is an important alternative fuel for diesel applications, but there is a tendency for biodiesel to increase nitrogen oxides (NO_x) emissions, which remains an issue in nonattainment areas. This study investigated the effect of using low blend level biodiesel fuels and fuel additives on emissions. Emissions from three B5 biodiesel fuels and six B20-soybean oil methyl ester (SME) with additive blends were evaluated as potential biodiesel formulations for California. B5-SME and B5-waste cooking oil methyl ester (WCOME) both showed measurable increases in NO_x emissions, while a B5-animal fat methyl ester (AFME) showed a slight reduction or no change in NO_x emissions compared to the CARB diesel. The B5-AFME blend also passed the criteria of the CARB diesel emissions equivalent certification test. Of the additives tested, only one provided reductions in NO_x emissions for the B20-SME blends, but the reductions were not enough to pass the CARB diesel emissions equivalent certification test at the B20 level. Biodiesel blends generally showed either reductions or no significant changes in particulate matter (PM), total hydrocarbon (THC), and carbon monoxide (CO) emissions.

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1. Introduction

There is a global interest in expanding the long term use of renewable fuels in transportation applications. The transportation sector represents one of the largest contributions to greenhouse gas and criteria emission inventories. One of the primary drivers for increasing the use of renewable fuels is the potential to reduce greenhouse gas emissions, such as carbon dioxide (CO_2), which contribute to global warming and climate change [1]. Studies have shown that the application of renewable fuels in the transportation sector can also decrease emissions of some criteria pollutants, such as particulate matter (PM) and carbon monoxide (CO), and help to improve air quality [2]. Increasing consumption of renewable fuels also reduces dependency on conventional fossil fuels, which ultimately have limited reserves.

In recent years, governmental agencies around the world have implemented legislation that targets growing the use of renewable fuels in the transportation sector. In the United States (U.S.), the energy independence and security act of 2007 targets the production of 36 billion gallons of biofuels in the U.S. by 2022. This target will be met mostly by corn and cellulosic ethanol, although other fuels will or could also contribute, such as biodiesel, renewable diesel fuel, and renewable gasoline [3]. The European Union (EU) has implemented several government mandates, such as the EU Renewable Energy Directive (2009/28/EC), which requires at least 10% of each Member State's transport fuel use to come from renewable sources (including biofuels) [4]. In Asia, recently several regulations have been approved and implemented. In Japan, the government announced a target to increase the annual production of biofuels from 175,000-cubic meters in 2010 to 500,000 cubic meters in 2017 [5]. In China, in August 2007, the National Development Reform Commission (NDRC) announced a Medium and Long Term Development Plan for Renewable Energy. In India, a National Policy on Biofuels was approved in September 2008, which mandates a 20% share of biodiesel and bioethanol shall be blended with diesel and gasoline by 2017 [6]. On a more regional level, California implemented the low carbon fuel standard (LCFS) in 2011 to promote the reduction of greenhouse gas emissions by targeting a reduction in the carbon intensity of transportation fuels by 10% by 2020 [7].

Fatty acid alkyl esters – most commonly Fatty Acid Methyl Esters (FAMEs) – often referred to as biodiesel are one of the most widespread renewable fuels. Commercially, biodiesel is produced by transesterification of triglycerides, the main constituent of vegetable oils, animal fats, and waste cooking oils. Transesterification occurs when triglycerides are mixed with an alcohol in the presence of an

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alkaline liquid catalyst, usually sodium or potassium methoxide. Biodiesel has several significant benefits aside from its value as a renewable fuel. For instance, biodiesel, either in its pure form or when blended with regular diesel fuel, can be used in existing diesel engines with no or minor engine modifications [1,8,9]. Many studies have shown that biodiesel blends reduce PM, CO, and total unburned hydrocarbon (THC) emissions compared to diesel fuel [1,10–14]. Biodiesel blends have been shown to reduce the overall life cycle emissions of CO_2, when evaluated using a total carbon life cycle analysis [1,15,16], although this can depend on a variety of factors, such as land use change and transportation [17,18]. A drawback in using biodiesel blends, however, is the potential to increase NO_x emissions compared to ultra-low sulfur diesel fuel (ULSD) [10–13,15,19].

NO_x is one of the primary precursors of ground-level ozone and secondary ambient PM formation. Over the years, increasingly more stringent regulations on diesel engines have been put in place, culminating with the U.S. EPA 2010 on-road heavy-duty engine standards that essentially require exhaust aftertreatment to reduce NO_x emissions. In states where a number of urban areas do not meet the national ambient air quality standards (NAAQS), such as California and Texas, further regulations of diesel fuel quality have also been put into place. These regulations require diesel fuel to meet a more stringent set of properties, or show emission equivalence to a 10% aromatic-hydrocarbon reference diesel fuel. As such, the California Air Resources Board (CARB) sets fuel specifications to ensure that fuels introduced into the state on a widespread basis do not adversely affect the State's air quality.

In recent years, many researchers have studied the impact of biodiesel blends on NO_x emissions [12,15,16,20–22]. Many of these studies have shown increases in NO_x emissions, although this trend is not consistent over all studies and all conditions [2,12,13,19,23,24]. Researchers have identified a variety of factors that could contribute to increased NO_x emissions for biodiesel [8,9,14]. Recent studies have suggested that the impacts of biodiesel on NO_x emissions are probably best explained by a combination of factors that interact differently under different conditions. Eckerle et al. suggested that both fundamental combustion effects, driven by fuel chemistry and fluid dynamics, and the effects of operating on lower energy content biodiesel must be considered to understand the impact of biodiesel on NO_x. They separated the combustion effect into flame temperature effects and ignition delay effects [25]. For the fundamental combustion effects, they emphasized the importance of the double bonds in biodiesel correlating with higher adiabatic flame temperatures, which can enhance NO_x formation through the thermal (Zeldovich) NO_x formation mechanism, as had previously been suggested by Banweiss et al. [26]. For the engine control effects, they evaluated the impact of increasing fuel volumetric flow rate needed for lower energy biodiesel on air–fuel ratio controls, exhaust gas recirculation (EGR) rate, and injection pressure and timing. Mueller et al. suggested that the presence of oxygen in biodiesel can also contribute to charge-gas mixtures that are closer to stoichiometric at ignition and in the standing premixed autoignition zone near the flame lift-off length. This in turn can lead to higher local and average in-cylinder temperatures and a shorter, more advanced combustion event, which would all contribute to increased thermal NO_x emissions [27]. This could also contribute to reduced radiant heat losses during combustion due to a reduction of PM emissions with biodiesel, and correspondingly higher combustion temperatures and higher NO_x emissions, as has also been suggested previously by Cheng et al. [28]. The Mueller et al. work did also find that although adiabatic flame temperature differences may contribute to NO_x differences, it did not appear to play a primary role in this regard [27]. In older engine technologies with pump line fuel injection systems, NO_x increases have been associated with the higher bulk modulus of biodiesel, which leads to a more advanced injection timing, which in turn increases fuel residence time and heat release near top dead center and raises the combustion temperature [29].

While studies investigating the impact of biodiesel blends on emissions, and specifically NO_x, are extensive and diverse, such studies have often been limited in terms of the number of engines and test replicates, with many of these studies focusing mainly on diesel fuels with relatively high sulfur and aromatic contents compared to the ones used in areas with more stringent air quality regulations, such as California and Texas [1,11–13,23]. Durbin et al. recently performed a comprehensive biofuel emission study focusing mainly on NO_x emissions [10,11]. They investigated the impact of biodiesel blends with diesel fuels meeting California Air Resources Board (CARB) requirements, which are characterized by low aromatic contents and relatively high cetane numbers. The results of their study showed that B20 and higher biodiesel blends would likely increase NO_x emissions in CARB diesel fuels. However, the results were less definitive at lower blend levels such as B5. The results also showed that the impacts of NO_x increases with biodiesel could be mitigated with combinations of blends with renewable and gas-to-liquid (GTL) diesel fuels, or with additives, such as di-tert-butyl peroxide (DTBP) [10,11]. The use of additives, in particular, has also shown some success in other studies, and could represent a viable and cost effective pathway to achieving NO_x neutral biodiesel blends [19,22,30].

The present study expands upon the earlier Durbin et al. work to more extensively study low level biodiesel blends and additives [10,11,31]. This study explores the emission impacts of different B5 biodiesel blends and B20 with additive blends under CARB's procedures for qualifying emission equivalent diesel fuel formulations. The emission equivalent diesel certification procedure is robust in that it requires at least twenty replicate tests on the reference and candidate fuels, providing the ability to differentiate small differences in emissions. For this study, preliminary tests were performed on biodiesel blends at a 5% concentration by volume (B5) prepared from three different methyl esters, including an animal fat methyl ester (AFME), a soybean oil methyl ester (SME), and a waste cooking oil methyl ester (WCOME). In addition, higher biodiesel blends made at a 20% concentration by volume (B20) with SME and treated with five different additive combinations were evaluated. Full certification tests were then performed on two of the B5 fuels, the B5-AFME and B5-WCOME, and one of the B20-SME with additive blends.

2. Material and methods

2.1. Test fuels and test engine

Nine different biodiesel blends were tested in this study. The biodiesel fuels were blended volumetrically at 5% and 20% levels, and are denoted as B5 and B20 throughout this paper. Additives were also added to the B20 blends. A CARB reference fuel was used as the baseline fuel to which the candidate fuel emissions were compared, and the base fuel with which the biodiesel was blended to produce the candidate fuels. The reference fuel was a 10% aromatic hydrocarbon diesel fuel meeting the CARB reference fuel specifications under title 13, California Code of Regulations (CCR), section 2282(g)(3). The specifications of the pure biodiesel feedstocks used in this program were all within ASTM 6751 standards for 100% biodiesel. The testing was conducted in two different segments for both the B5 and B20 fuels. First, preliminary or scoping testing was conducted on selected biodiesel blends for comparison. Full certification testing was then performed on the candidate fuels from the preliminary testing that showed the most promise.

Three B5 biodiesel blends were tested in the first phase of this study, one with a SME, one with an AFME, and one with a WCOME. The B5 blends are denoted as B5-SME, B5-AFME, and B5-WCOME throughout this paper. The feedstocks for these biodiesel blends were selected not only to represent some of the more widely used feedstocks for biodiesel production in the U.S., but also to span a wide range of biodiesel properties. It should be noted that currently, 40% or more of U.S. biodiesel fuel is made from mixed feedstocks [32], so the feedstocks were also selected to try to span a relatively wide range of biodiesel properties that might be found in the biodiesel marketplace.

Six SME B20 blends were tested in the second phase of the study, including five with additives and one without an additive. The SME, denoted as B20-SME, was used as the base fuel for all the B20 testing. The additives are denoted as additive-A, additive-B, additive-C, additive-D, and additive-E.

Table 1 shows some key properties of the CARB reference fuels, the neat biodiesel fuels, and the biodiesel blends. Note that two different batches of reference fuel from the same supplier were used in this study. One was used during the B5 testing and preliminary testing of the Additive A and Additive B B20-SME blends, and the other was used for the rest of B20-SME blend preliminary and certification testing. It should be noted that the properties provided for the B20-SME and B5-SME blends are arithmetic averages of the corresponding properties for the CARB reference fuel and the pure SME based on their relative volume, mass, or energy fractions. More detailed listings of all the properties of the CARB reference fuels, the neat biodiesel fuels, and the biodiesel blends are also provided in the supporting information.

The engine that was used in this study was an in-line six cylinder, 10.8 L, 2006 model year Cummins ISM 370 engine with a common rail fuel injection system, a turbocharger, a charge air cooler, and exhaust gas recirculation (EGR). The family emission limit certification level for this engine is 2.4 g/bhp·hr for NO_x + NMHC. Note that this engine was not equipped with any exhaust aftertreatment. The specifications of the engine are provided in the supporting information.

2.2. Test cycle and test matrix

All testing were conducted in accordance with the Federal Test Procedure (FTP) for heavy-duty engines [33]. The testing for the preliminary and certification emission testing was conducted using one of the hot start sequences described under 13 CCR 2282(g)(4)(C)1.b Alternative 1. The daily test sequence was performed as RC CR RC CR, where “R” is the reference fuel and “C” is the candidate fuel. For the preliminary testing, only a single day using this sequence was conducted for each of the candidate fuels. For the certification testing, this sequence was continued for a period of at least 5 days until a minimum of twenty individual hot start exhaust emission tests with an equal number of morning and afternoon tests were completed with each fuel. The test sequence for the certification testing is presented in the supporting information. An engine map was conducted at the beginning of each test day on the reference fuel. This provided consistent preconditioning for each test day. The engine map on the reference fuel for the first day for a given test sequence was used for all subsequent emission testing on both the reference and candidate fuels.

2.3. Emission testing

The engine emission testing was performed in the University of California, Riverside's (UCR's) College of Engineering-Center for Environmental Research and Technology's (CE-CERT's) heavy-duty engine dynamometer laboratory. This laboratory is equipped with a 600-hp General Electric DC electric engine dynamometer.

For all tests, standard emission measurements of THC, CO, NO_x, PM, and CO_2 were made. The emission measurements were made using the standard analyzers in CE-CERT's heavy-duty Mobile Emissions Laboratory (MEL) trailer [34,35]. Fuel consumption was determined from these emission measurements via the carbon balance method using the densities and carbon weight fractions from the fuel analysis.

As a part of the certification testing procedure, soluble organic fraction (SOF) analysis was performed on PM filters collected during the B5-AFME and B5-WCOME certification testing. For the B5-AFME testing, PM filters from each test were analyzed for SOF. For the B5-WCOME testing, only 3 SOF analyses were performed for both the CARB reference fuel and B5-WCOME since this blend did not pass the NO_x

Table 1
Properties of fuels and blendstocks.

Property	ASTM test method	Units	AFME	WCOME	SME	CARB batch 1	CARB batch 2	B5-AFME	B5-WCOME	B5-SME	B20-SME
Sulfur	ASTM D5453	Ppm	6.5	11.1	1.1	4.7	None detected	4.5	5.3	NA	NA
Cetane number	ASTM D613		61.1	54.6	49.2	53.1	48.4	61	52.2	NA	NA
Heating value	ASTM D240	BTU/lb	17,133	17,076	17,140	19,689	19,689	19,661	19,649	19,568	19,200
API gravity @ 60 °F	ASTM D4052		30.20	28.40	28.43	37.2	38	38.5	38.2	36.76	35.4
Specific gravity @ 60 °F	ASTM D4052		0.8750	0.8851	0.8848	0.839	0.836	0.8326	0.8339	0.841	0.85
Carbon	ASTM D5291	Wt.%	76.19	76.67	77.10	85.80	85.80	85.78	85.85	85.4	84.1
Hydrogen	ASTM D5291	Wt.%	12.28	11.98	11.85	13.61	13.61	13.8	13.82	13.5	13.3
Carbon unit per energy		lbs. carbon/BTU	4.45×10^{-5}	4.49×10^{-5}	4.50×10^{-5}	4.36×10^{-5}	4.36×10^{-5}	4.36×10^{-5}	4.37×10^{-5}	4.37×10^{-5}	4.39×10^{-5}

B5-SME and B20-SME properties are the arithmetic averages of B100-SME and CARB reference fuel.

certification criteria. For these three analyses on each fuel, filters from 12 different tests were aggregated into 3 different groups.

For SOF analysis, the filters were weighed prior to extraction with a Mettler Toledo MT5 electro microbalance with ±0.001 mg sensitivity. The polyethylene ring was carefully removed from the exposed Teflon-membrane filters (47 mm) prior to weighing. The filters were subsequently extracted with dichloromethane followed by hexane in an Accelerated Solvent Extractor (Dionex 3000), dried, reconditioned and re-weighted to determine the SOF. A combination of dichloromethane with hexane was used for the extraction, since it gives good recovery for aliphatic hydrocarbons, cycloalkanes, PAH, hopanes, and steranes, i.e., the classes of compounds that are prevalent in motor vehicle emissions.

3. Results and discussion

The results of the preliminary and certification testing for each emission component are presented in Figs. 1–5. These figures represent the average of all test runs done on a particular fuel for a specific test segment. The error bars represent one standard deviation on the average value. The CARB reference fuel results are presented separately for the different test days for the preliminary testing and for the different test periods for the certification testing, and are shown with different bars in the figures, denoted as CARB vs. the blend name. Tables 2 and 3 show the average emission values, the percentage differences for the different biodiesel fuels compared to the CARB reference fuel, and the associated p-values for statistical comparisons using a 2-tailed, 2-sample, equal-variance *t*-test. The results of this study were considered to be statistically significant for p values ≤ 0.05, and marginally statistically significant for $0.05 \leq p$ values < 0.1. The pass/fail criteria for the certification testing are based on additional statistical analysis for NO_x, PM, and SOF. More detailed results for the NO_x, PM, and SOF for the certification testing, and the corresponding statistical analysis for the certification test criteria, are provided in the supporting information.

3.1. NO_x emissions

The NO_x emission results for the B5 and B20 are presented in Fig. 1 on a gram per brake horsepower hour (g/bhp-hr) basis. The preliminary B5 testing showed statistically significant 1.2–1.3% increases with the B5-SME and B5-WCOME biodiesel blends compared to the CARB reference fuel. The preliminary B5-AFME emission results, on the other hand,

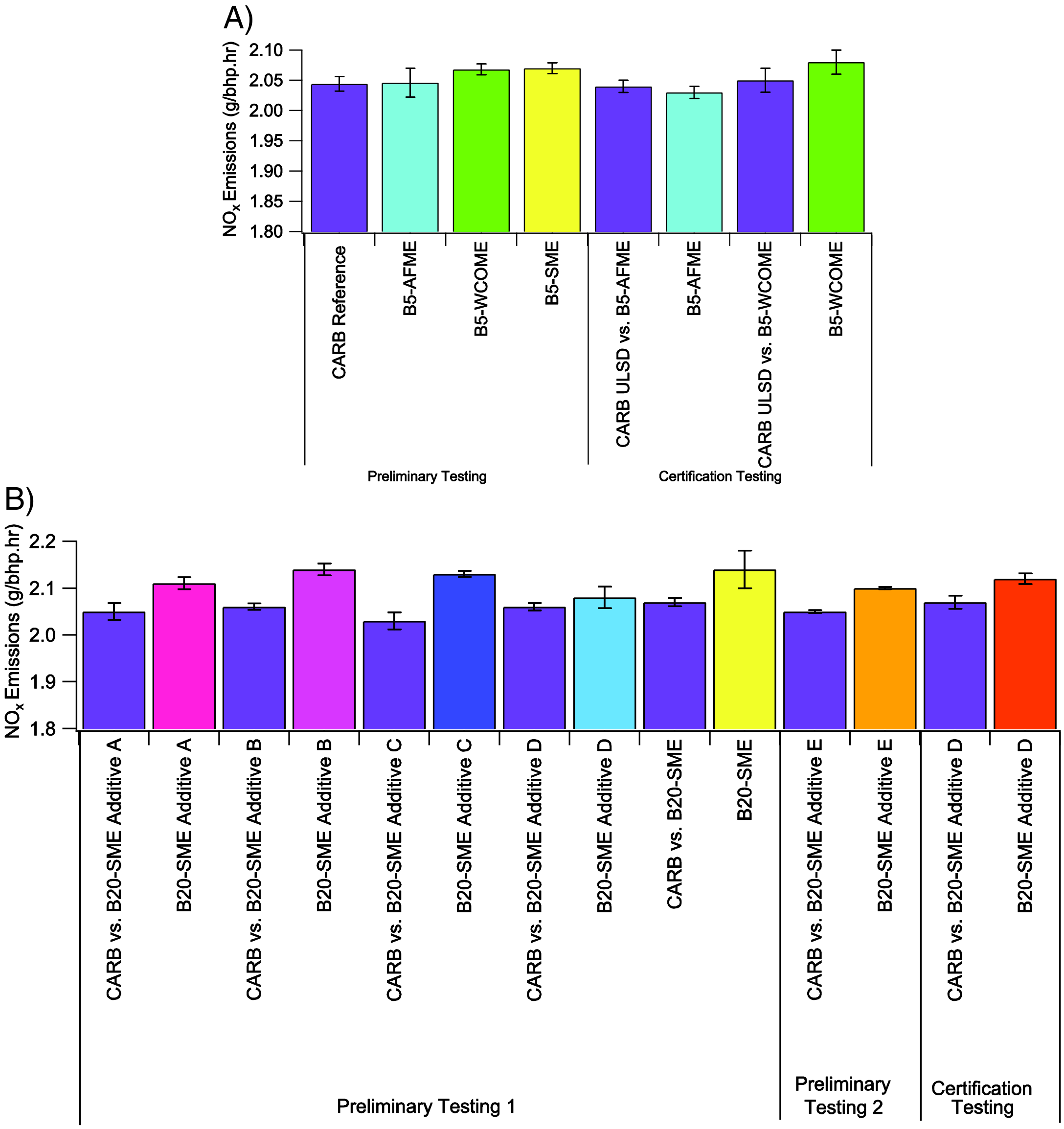

Fig. 1. Average NO_x emission results for the preliminary and certification testing A) B5, B) B20 with additives.

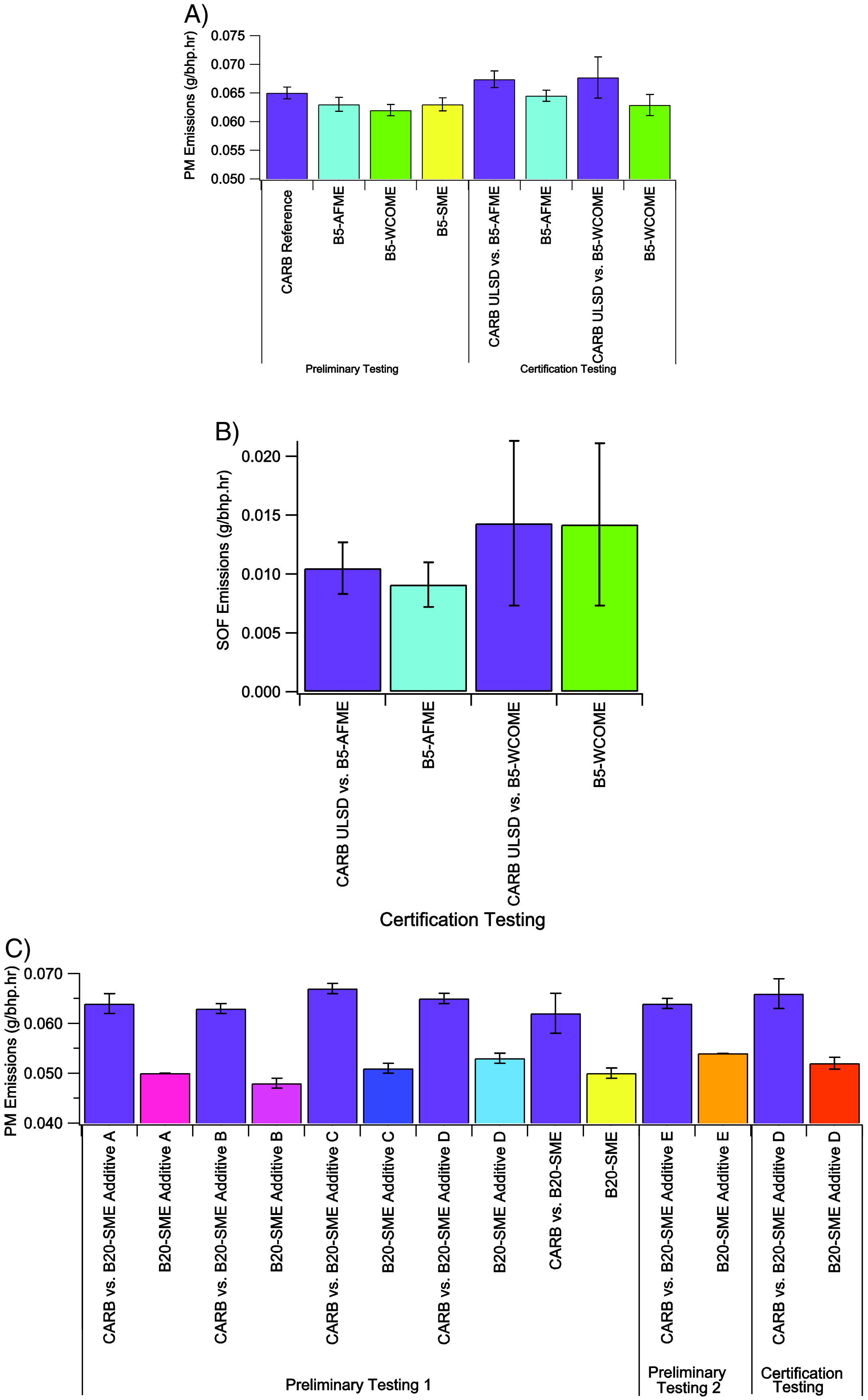

Fig. 2. Average PM and SOF emission results for the preliminary and certification testing A) B5, B) B5, C) B20 with additives.

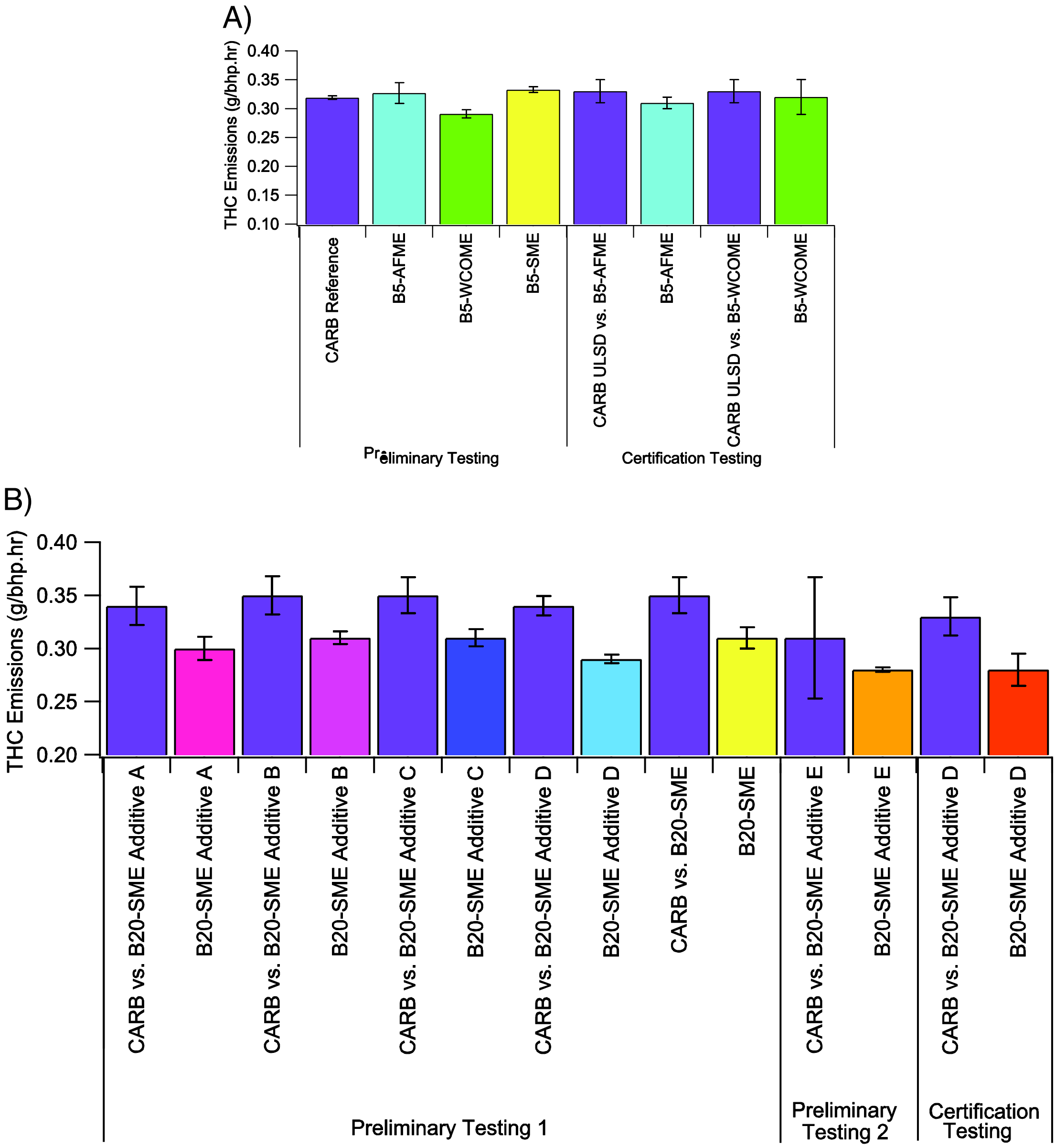

Fig. 3. Average THC emission results for the preliminary and certification testing A) B5, B) B20 with additives.

did not show any statistical differences in NO_x compared to the CARB reference fuel. Therefore, this fuel blend was considered the most viable candidate fuel for the actual certification testing.

The emission equivalent B5 certification testing was performed on B5-AFME and B5-WCOME blends. The B5-AFME emission results of the certification testing showed a statistically significant 0.5% reduction in NO_x emissions compared to the CARB reference fuel. The B5-WCOME emission results, on the other hand, showed a statistically significant 1.0% increase in NO_x emissions compared to the CARB reference fuel. Based on the certification testing results, the B5-AFME passed the certification criteria for NO_x emissions, while the B5-WCOME failed. The results of the B5 testing are consistent with previous studies showing that the magnitude of NO_x emission increases can change with the biodiesel feedstock, with more saturated feedstocks, such as animal tallow, often showing smaller increases [11,14,16]. Less saturated biodiesel feedstocks have higher C/H ratios and would have a stoichiometry that is more oxidizing in the premixed autoignition zone. Mueller et al. showed charge air mixtures that are closer to stoichiometric at ignition and in the standing premixed autoignition tend to produce higher local and average in-cylinder temperatures, lower radiative heat losses, and a shorter more advanced combustion, all factors that would be expected to increase thermal NO_x emissions [27]. It is worth noting that while candidate fuels must pass certification criteria for NO_x, PM, and SOF, for biodiesel blends NO_x emissions were considered the most important pollutant for this testing, since other pollutants generally tend to decrease for biodiesel blends.

NO_x emission results for the B20 preliminary testing showed a statistically significant 1.2–5.1% increase with B20-SME with additive blends compared to the CARB reference fuel. In comparison, NO_x emission results for the B20 SME blend without additives showed an increase of approximately 3.3%. The B20-SME Additive D blend from the preliminary testing showed the lowest increase in NO_x emissions (1.2%) compared to the other B20-SME with additive blends. The B20-SME Additive D blend was also the only additive blend that showed a marginally statistically significant reduction in NO_x emissions compared to the B20-SME based biodiesel without additives. It should be noted that there was a range of approximately 2% in the daily average NO_x emissions for the CARB reference fuel between the days with the

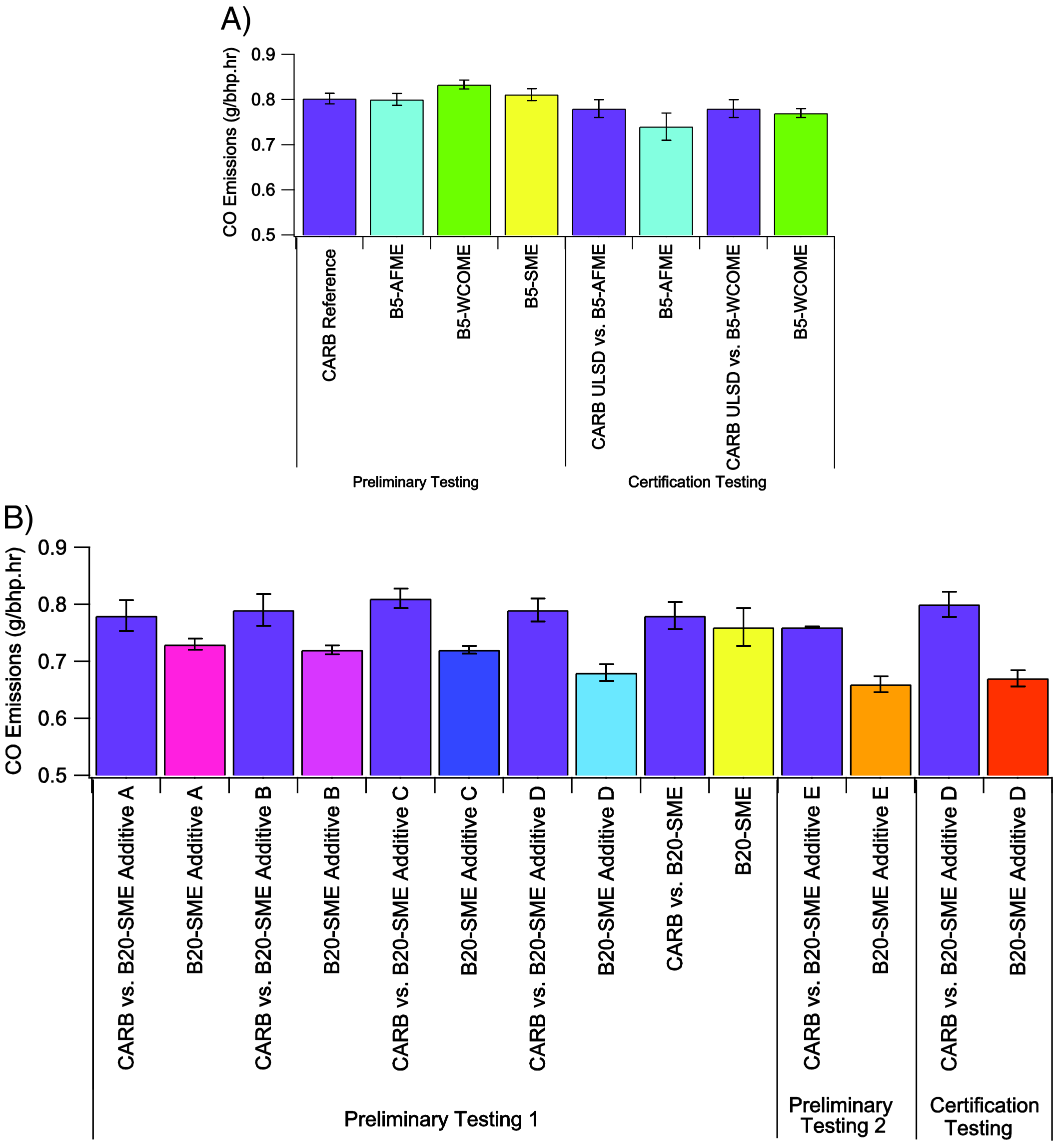

Fig. 4. Average CO emission results for the preliminary and certification testing A) B5, B) B20 with additives.

highest and lowest NO_x emissions, so these data cannot be taken as a definitive comparison of the performance between the individual additives themselves. The B20-SME Additive D blend was selected for the actual certification testing on the basis of the preliminary test results. The more comprehensive certification emission testing results for the B20-SME Additive D blend showed a 2.5% statistically significant increase in NO_x emissions over the CARB reference fuel. Therefore, the B20-SME Additive D blend did not pass NO_x emission criteria of the certification testing.

Although many studies have shown NO_x increases with biodiesel, there are still questions as to the actual impact of biodiesel on NO_x emissions at B20 and lower levels. Broad based literature reviews have shown NO_x increases in some cases [10–13] and considerable variability between studies in others [15,19,23], making it difficult to definitely conclude that biodiesel increases NO_x emissions at B20 and lower levels. Evaluating a more limited subset of studies using CARB-like diesel fuels shows a stronger tendency for NO_x increases at the B20 level, probably because CARB diesel is a lower NO_x base fuel that will accentuates the contrast with the biodiesel blends. In evaluating a range of heavy-duty engine dynamometer studies with B20 SME biodiesel in CARB-like diesel fuel, Hajbabaei et al. found average increases of 4.2% for B20-SME, comparable to values seen in this study [11].

Studies characterizing the emission impacts of biodiesel at levels lower than B20 have been even more limited. Hajbabaei et al. showed mixed results for B5 blends with CARB diesel depending on the engine type, biodiesel type, and number of replicates. For SME B5 blends, however, it was found that some type of mitigation, either in the form of an additive or blending with another renewable diesel, was needed to achieve NO_x neutrality compared to CARB diesel [11]. Nikanjam et al. did not show significant differences in NO_x with B5, although more limited replicates were used in that study [36]. At the B10 level, data are even more limited, with a few studies showing increases for B10 compared to CARB diesel [10,11,37]. The results of this study suggest that small but detectable increases can be seen for B5 blends with CARB diesel when a sufficiently robust test matrix is used, although increases were not seen for the AFME B5 blend. This is consistent with other studies showing that more saturated biodiesel fuels, such as AFME, show smaller increases in NO_x emissions [2,12,19,24].

Several previous studies have shown that NO_x neutral biodiesel blends can be obtained using additive blends with either DTBP or 2-EHN. Some of these earlier studies used older engines or non-CARB-like base fuels, however, which would make them less comparable with the present study [19,22,30,38,39]. McCormick et al. investigated the effect of using cetane improver additives, such as DTBP, 2-EHN, and the antioxidant additive tert-butyl hydroquinone (TBHQ). They showed that these additives can reduce NO_x emission increases to some extent, however, the magnitude of the reductions was dependent on the base fuel aromatic content [39]. Several other authors have tested DTBP and 2-EHN additives and observed some potential for mitigating NO_x increases with biodiesel blends [40–45]. The effect of cetane improvers tends to be less or negligible in newer engine technologies [2,40]. The results of a study performed by Durbin et al. were mixed for different additives tested on a different 2006 Cummins ISM engine, with a 1% DTBP additive blend showing NO_x neutrality for B20 and lower blends, while other tests using an 2-EHN additive blend were not successful at mitigating NO_x emissions even at blend levels as low as 5% [10,11]. Some of the specific additives used in this study have also shown more substantial reductions in other studies of a more limited scope [46,47].

Other methods can also be utilized to achieve NO_x neutrality. Szybist et al. in another study achieved NO_x neutral formulations with B20 biodiesel blends by altering biodiesel chemical composition to achieve lower iodine number. They showed that the NO_x impact can be neutralized with shifting the compressibility of the biodiesel fuel [48]. Another alternative could be reformulating petroleum diesel to provide a base fuel that is sufficiently low in emissions that even after the addition of biodiesel at a 5% or 20% level a NO_x neutral formulation could be achieved. Engine control strategies such as EGR fraction, injection pressure are other factors that can be used to mitigate NO_x emission increases with biodiesel [49,50], although such measures would likely be difficult to implement across a wide region in support of fuel regulations.

3.2. PM and SOF emissions

The PM emission results for the B5 and B20 testing and SOF emission results for the B5 certification testing are presented in Fig. 2 on a g/bhp-hr basis. PM emissions showed consistent, statistically significant reductions for both the B5 and B20 blends. For the B5 blends, the reductions ranged from 4 to 7% over the preliminary and certification

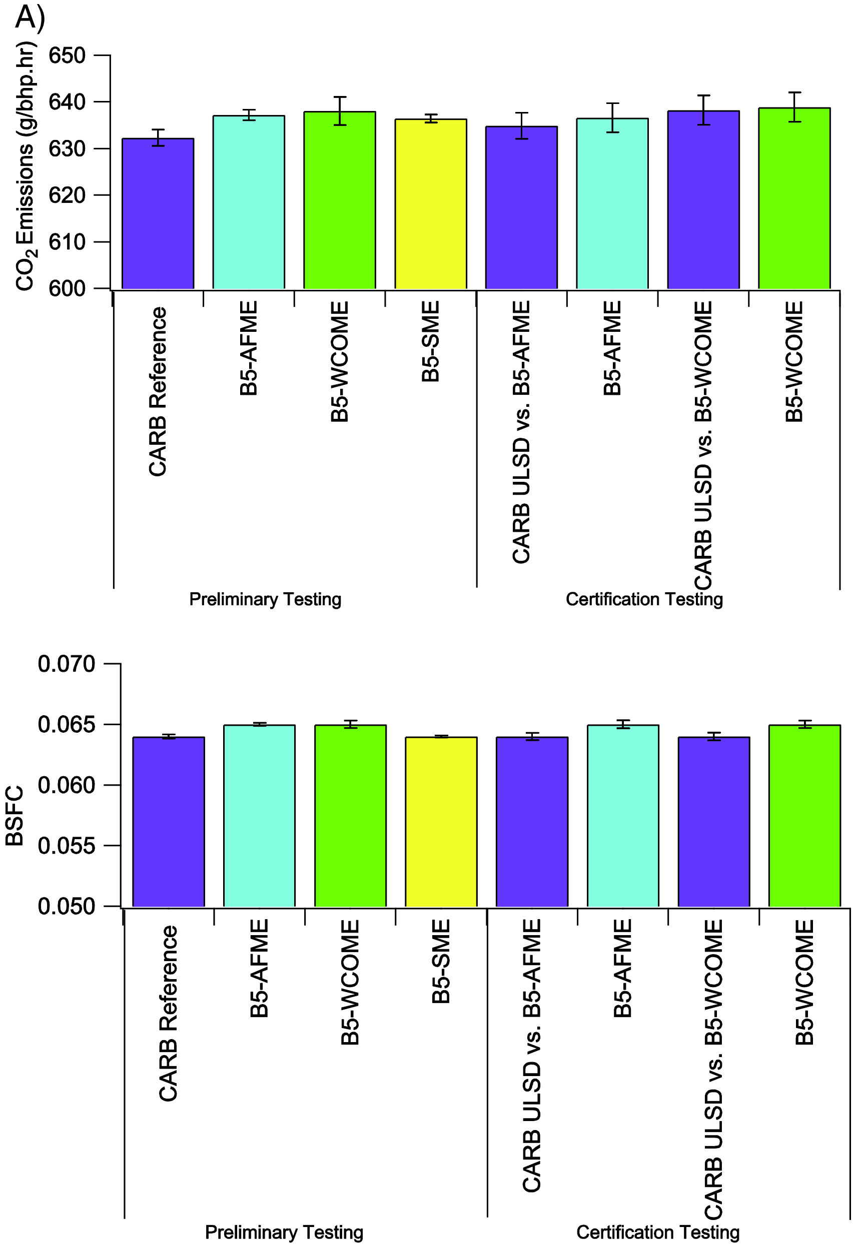

Fig. 5. Average CO_2 emission and BSFC results for the preliminary and certification testing A) B5, B) B20 with additives.

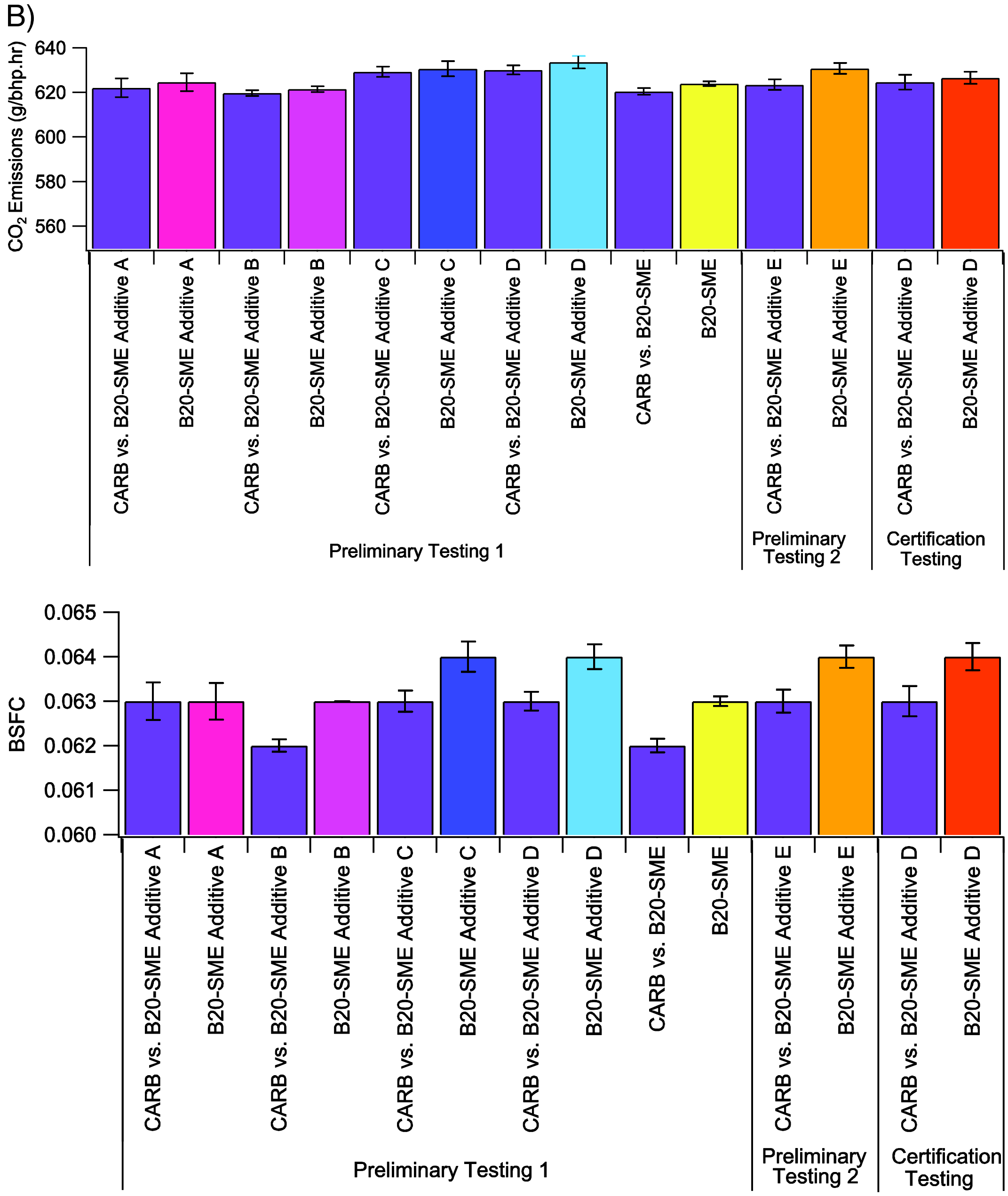

Fig. 5 (*continued*).

testing. Larger reductions, ranging from 15.7 to 24.7%, were found for the B20 with additive blends and B20-SME compared to the CARB reference fuel for preliminary and certification testing. No statistical differences were found between PM emissions of B20 with or without additives, indicating that the additives did not appear to provide additional PM benefits beyond that obtained for the biodiesel itself. For the certification test, the reduction in PM emissions was 20.6% for the B20-SME Additive D blend. The B20-SME Additive D blend and both the B5 blends passed the PM emission criteria of the certification testing.

SOF overall represented a relatively small fraction of the total PM mass, ranging from 14 to 23%. The B5-AFME emission results showed a statistically significant reduction in SOF compared to the CARB reference fuel. The decrease in SOF emissions for the B5-AFME was actually greater on a percentage basis than the reduction in total PM mass for the certification test. Based on the certification testing results, the B5-AFME passed the certification criteria for SOF. The B5-WCOME emission results showed no difference compared to the CARB reference fuel for SOF. The greater variability for the B5-WCOME results is probably due to the limited number of SOF analyses conducted for the B5-WCOME certification test, or the fact that the samples were aggregated from several individual tests. Since the B5-WCOME results were not analyzed for all of the samples, these results were not analyzed in terms of pass/fail for the certification test. SOF results were not analyzed for the B20 certification test since it did not pass the certification criteria for NO$_x$ emissions.

Consistent with many previous studies, PM emissions decreased with increasing biodiesel levels [11–14,21]. PM reductions with biodiesel blends are generally attributed to the presence of oxygen in the biodiesel and its impact on reducing excessively rich zones during combustion [11–14,21,22,30,51,52]. In other studies, adding additives to biodiesel blends has generally not shown significant additional benefits with respect to PM, similar to the present study [10,22,30,51,52], with the exception of some tests that appear to be outliers [46,47].

Table 2
Emissions (g/bhp-hr) and BSFC (gal/bhp-hr) percentage differences between the B5 biodiesel blends and the CARB reference fuel for the preliminary and certification testing.

	Fuel type	NO_x emissions			PM emissions			SOF emissions			THC emissions		
		Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values
Preliminary testing ($n = 6$)	CARB	2.04			0.065						0.319		
	B5-AFME	2.05	0.1%	0.844	0.063	−5.9%	**0.003**				0.327	2.4%	0.367
	B5-WCOME	2.07	1.2%	**0.020**	0.062	−3.8%	**0.000**				0.291	−8.8%	**0.000**
	B5-SME	2.07	1.3%	**0.001**	0.063	−4.2%	**0.001**				0.333	4.3%	**0.001**
Certification testing ($n = 20$)	CARB	2.04			0.067			0.0105			0.330		
	B5-AFME	2.03	−0.5%	**0.006**	0.065	−4.2%	**0.000**	0.0091	−13.6%	**0.036**	0.314	−4.8%	**0.001**
	CARB	2.05			0.068			0.0143			0.331		
	B5-WCOME	2.08	1.0%	**0.0001**	0.063	−7.0%	**0.000**	0.0142	−0.2%	0.990	0.324	−2.1%	0.330

	Fuel type	CO emissions			CO_2 emissions			BSFC		
		Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values
Preliminary testing	CARB	0.802			632.30			0.0637		
	B5-AFME	0.800	−0.3%	0.761	637.21	0.8%	**0.000**	0.0649	2.0%	**0.000**
	B5-WCOME	0.833	3.8%	**0.011**	638.08	0.9%	**0.000**	0.0646	1.4%	**0.000**
	B5-SME	0.811	1.1%	0.272	636.45	0.7%	**0.002**	0.0641	0.6%	**0.000**
Certification testing	CARB	0.783			634.88			0.0639		
	B5-AFME	0.737	−5.9%	**0.000**	636.58	0.3%	0.077	0.0645	1.0%	**0.000**
	CARB	0.779			638.2			0.0642		
	B5-WCOME	0.765	−1.8%	**0.002**	638.9	0.1%	0.464	0.0646	0.6%	**0.000**

Bold: statistically significant; underline: marginally statistically significant.
n = number of replicates.

Previous studies have generally shown higher SOF emissions for biodiesel blends compared to either regular diesel fuel or low sulfur diesel fuel. However, most of these studies were performed on U.S. Federal diesel fuels as the base fuel, as opposed to a lower aromatic CARB diesel, and typically were characterized for higher biodiesel blend levels [8,53]. The increase in SOF emissions with biodiesel has been attributed to the higher boiling point or lower volatility of biodiesel fuel, which contributes to increased condensation of unburned hydrocarbons on the particle's surface [54,55]. This observation might vary from study to study due to testing conditions and methods for PM sampling [56]. Karavalakis et al. categorized the SOF emissions from biodiesel blends in four groups including methyl esters (mainly biodiesel components), oxygenated chemicals (chemicals with oxygen but not methyl esters), alkanes and alkenes, and aromatic species. Based on their study, SOF from B5 blends primarily consist of straight-chain alkanes, aromatic hydrocarbons, and aliphatic hydrocarbons like the regular diesel fuel [57]. This is consistent with the results of this study which showed a comparable level of SOF for both CARB low aromatic reference fuel and B5 biodiesel blends.

3.3. THC emissions

The THC emission results for the B5 and B20 testing are presented in Fig. 3 on a g/bhp-hr basis. For the B5 certification testing, the emission testing results for both blends showed reductions in THC compared to the CARB reference fuel. The reduction seen for B5-WCOME was not statistically significant, however. THC results were mixed for the preliminary testing, with the B5-WCOME emission results showing a statistically significant 8.8% reduction in THC, while the B5-SME emission results showed a slight statistically significant increase in THC compared to the CARB reference fuel. The latter observation is opposite to that seen in other studies [2,10,12,13,23,24] and might be due to the low values of THC emissions over all the fuel blends or limited number of tests done in the preliminary testing. The B5-SME preliminary testing results may have been an anomaly for that particular day. The stronger THC trends for the certification tests compared to preliminary tests are probably due to the more robust test matrix and the greater number of test replicates. It should be noted that THC emissions are not part of the pass/fail criteria for the full certification test.

THC emission results for both the preliminary and certification testing of B20 blends showed consistent statistically significant 10.8–16.8% reductions for the B20 and B20 additive blends. Only the reduction in THC emission results for B20-SME Additive E compared to CARB reference fuel was not statistically significant, which might be due to the limited number of tests that were performed for this specific blend. For the certification test, the reduction in THC emissions was 16.8% for the B20-SME Additive D blend.

The trends of reduced THC emissions for biodiesel and biodiesel additive blends are consistent with the results seen in other studies [2,10,12,14,23,24]. This can be attributed to the presence of oxygen in the biodiesel, which contributes to more complete combustion when biodiesel blends are used [12–15,25]. Durbin et al. showed that additives in conjunction with B20 blends provided greater reductions in THC emissions compared to the B20-SME baseline fuel alone [10]. The same trend was also seen for the B20-SME additive blends for the present study, with either equal or greater reductions in THC emissions seen for the B20-SME additive blends compared to the B20-SME blend. In other studies, adding additives to biodiesel blends has generally either shown modest additional benefits or no significant additional benefits with respect to THC [10,22,30,51,52], with the exception of some studies with a more limited scope [46].

3.4. CO emissions

The CO emission results for the B5 and B20 testing are presented in Fig. 4 on a g/bhp-hr basis. The results for both B5 blends for the certification testing showed statistically significant reductions in CO emissions compared to the CARB reference fuel in the range of 2–6%. It should be noted that CO emissions are not part of the pass/fail criteria for the full certification test. The results of the B5 preliminary testing did not show consistent trends for CO emissions over all the biodiesel fuel blends. Interestingly, emission testing results showed a statistically significant increase of 3.8% in CO emissions for B5-WCOME compared to the CARB reference fuel in the preliminary testing. This is contrary to most studies in the literature, which generally show CO reductions with biodiesel [12,14,15,58]. This suggests that B5-WCOME preliminary testing results may have been an anomaly for that particular day.

Table 3
Emissions (g/bhp-hr) and BSFC (gal/bhp-hr) percentage differences between the B20 additive biodiesel blends and the CARB reference fuel for the preliminary and certification testing.

	Fuel type	NO_x emissions			PM emissions			THC emissions		
		Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values
Preliminary testing 1 (n = 4)	CARB vs. B20-SME Additive A	2.05			0.064			0.343		
	B20-SME Additive A	2.11	3.1%	**0.000**	0.050	−21.3%	**0.000**	0.301	−12.3%	**0.012**
	CARB vs. B20-SME Additive B	2.06			0.063			0.349		
	B20-SME Additive B	2.14	3.8%	**0.000**	0.048	−22.8%	**0.000**	0.314	−9.9%	**0.028**
	CARB vs. B20-SME Additive C	2.03			0.067			0.353		
	B20-SME Additive C	2.13	5.1%	**0.000**	0.051	−24.7%	**0.000**	0.305	−13.7%	**0.002**
	CARB vs. B20-SME Additive D	2.06			0.065			0.339		
	B20-SME Additive D	2.08	1.2%	0.100	0.053	−18.0%	**0.000**	0.287	−15.5%	**0.000**
	CARB vs. B20-SME	2.07			0.062			0.353		
	B20-SME	2.14	3.3%	**0.016**	0.050	−20.7%	**0.001**	0.315	−10.8%	**0.008**
Preliminary testing 2 (n = 3)	CARB vs. B20-SME Additive E	2.05			0.064			0.311		
	B20-SME Additive E	2.10	2.5%	**0.000**	0.054	−15.7%	**0.000**	0.277	−10.9%	0.337
Certification testing (n = 20)	CARB vs. B20-SME Additive D	2.07			0.066			0.334		
	B20-SME Additive D	2.12	2.5%	**0.000**	0.052	−20.6%	**0.000**	0.278	−16.8%	**0.000**

	Fuel type	CO emissions			CO2 emissions			BSFC		
		Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values	Ave. (g/bhp·hr)	% diff vs. CARB	p-Values
Preliminary testing 1	CARB vs. B20- SME Additive A	0.782			622.0			0.0628		
	B20-SME Additive A	0.728	−6.9%	**0.019**	624.6	0.4%	0.895	0.0635	1.0%	0.103
	CARB vs. B20-SME Additive B	0.793			619.7			0.0624		
	B20-SME Additive B	0.723	−8.9%	**0.009**	621.4	0.3%	0.156	0.0632	1.2%	**0.001**
	CARB vs. B20-SME Additive C	0.815			629.2			0.0634		
	B20-SME Additive C	0.717	−12.0%	**0.000**	630.6	0.2%	0.502	0.0641	1.1%	**0.013**
	CARB vs. B20-SME Additive D	0.795			630.0			0.0634		
	B20-SME Additive D	0.679	−14.5%	**0.000**	633.5	0.6%	0.091	0.0644	1.5%	**0.002**
	CARB vs. B20-SME	0.780			620.4			0.0625		
	B20-SME	0.755	−3.1%	0.278	623.9	0.6%	**0.008**	0.0634	1.5%	**0.000**
Preliminary testing 2	CARB vs. B20-SME Additive E	0.765			623.4			0.0628		
Certification testing	B20-SME Additive E	0.656	−14.2%	**0.002**	630.7	1.2%	**0.047**	0.0641	2.1%	**0.011**
	CARB vs. B20-SME Additive D	0.799			624.6			0.0629		
	B20-SME Additive D	0.672	−15.9%	**0.000**	626.5	0.3%	0.062	0.0636	1.2%	**0.000**

Bold: statistically significant; underline: marginally statistically significant.
n = number of replicates.

CO emission results for B20 testing showed consistent trends of reductions over all the B20 additive fuel blends. These reductions ranged from 6.9 to 15.9% compared to CARB reference fuel for both the preliminary and certification testing. The B20-SME blend CO emission results did not show statistically significant differences compared to the CARB reference fuel, however. For the certification test, the reduction in CO emissions was 15.9% for the B20-SME Additive D blend.

Previous studies have generally shown reductions in CO for biodiesel blends, with greater reductions found for higher level blends [12,14,15,58]. CO reductions for biodiesel are generally attributed to the oxygen content in the biodiesel that promotes more complete combustion. Similar testing on another 2006 Cummins ISM, however, also did not show strong effects for SME biodiesel blends ranging up to 100%, although CO emission benefits were seen for biodiesel blends with an AFME feedstock [10]. Similar to the current study, Durbin et al. found that additives can provide additional benefits in CO emissions beyond what would otherwise be achieved by biodiesel alone, although this was only studied for a SME blend [10]. In other studies, adding additives to biodiesel blends has generally either shown modest additional benefits or no significant additional benefits with respect to CO [10,22,30,51,52], with the exception of some studies with a more limited scope [46].

3.5. CO_2 emissions

The CO_2 emission results for the B5 and B20 testing are presented in Fig. 5 on a g/bhp-hr basis. The preliminary testing results for all the B5 blends showed statistically significant 0.7–0.9% increases of CO_2 emissions compared to the CARB reference fuel. The differences in the CO_2 increases for the more robust B5 certification testing were smaller and less statistically significant. CO_2 emission results showed increases for some of the B20 additive blends, but not for others. These increases were in the range of 0.2–1.2%. It should be noted that since the day to day variability in CO_2 emissions for the CARB reference fuel was approximately 1.5% over the course of the testing, these results should not be considered as a definitive comparison between the performance of specific additives. CO_2 emissions are not part of the emissions considered in the pass/fail criteria for the certification test.

Previous studies have shown increases in exhaust CO_2 emissions with biodiesel, but this has generally been seen for higher biodiesel blend levels [12,14,15,58–60]. The increases in CO_2 emissions could be related to the generally higher carbon content per unit of energy for biodiesel compared to typical diesel fuel. As shown in Table 1, the neat biodiesel fuels for the present study had higher carbon contents per unit of energy than the CARB reference fuel. There was approximately a 0.46% difference in the carbon content per unit energy between the CARB reference fuel and the B20-soy, as shown in Table 1. This is comparable to the marginally statistically significant difference in CO_2 emissions seen for the B20-additive certification test. There were essentially no differences in the carbon contents per unit of energy for the B5 blends compared to the reference fuel, however. It should be emphasized that an increase in exhaust CO_2 emissions for biodiesel does not imply that the use of biodiesel has a negative impact on greenhouse gas emissions. The actual contribution of different fuels towards total greenhouse gas emissions would need to be assessed through a full lifecycle analysis, which would account for the emissions attributed to harvesting, extracting, producing, and associated land use changes for the various fuels [8].

3.6. Brake specific fuel consumption

The brake specific fuel consumption (BSFC) results for the B5 and B20 testing are presented in Fig. 5 on a gal/bhp-hr basis. The BSFC results for both B5 blends tested during certification testing showed 0.6–1.0% increases in fuel consumption compared to the CARB reference fuel that were statistically significant. BSFC for the B5 blends was 0.6–2.0% higher in the preliminary testing compared to the CARB reference fuel. The B20 SME and B20-SME with additive blends of both preliminary and certification testing showed 1.0–2.1% higher BSFC compared to the CARB reference fuel. For the B20 certification test, the increase in BSFC emissions was 1.2% for the B20-SME Additive D blend. Note that BSFC is not a pass/fail criteria consideration for the certification test.

The BSFC result is directionally consistent with the results of previous studies, although BSFC impacts are usually more readily apparent at higher blend levels [12,14,15,58–60]. In the present study, although there are differences in the energy contents of the pure biodiesel compared to the CARB reference as shown in Table 1, the differences in the energy contents of the B5 blends and the CARB reference fuel are very minor. For the B20-SME, the increases in BSFC for the testing were slightly less than the 2.6% difference in the energy content between the CARB reference fuel and B20-SME used in this fuel.

4. Conclusions

As the use of renewable fuels continues to expand in the transportation sector, it is important to continue to evaluate their overall impact on ambient air quality. Currently, biofuels are being integrated into diesel fuel markets at levels of typically B20 and lower. Although our understanding of the increase in NO_x with biodiesel has improved over the last few years [8,9,14,27], the impacts of biodiesel at levels below B20 on NO_x emissions and emission inventories have not been definitively characterized to date. In this study, the impacts of B20 and lower blends were evaluated for a 2006 Cummins ISM engine on a heavy-duty engine dynamometer over a relatively robust test matrix designed to distinguish small differences in NO_x emissions. Overall, the results are consistent with our previous work and the work of others that the impact of biodiesel on NO_x emissions might be a more important consideration when blended with CARB diesel or similar fuels, and that some form of NO_x mitigation might be needed for biodiesel blends with such fuels. The results showed definitive NO_x increases at the B20 level, as well as increases at the B5 level, depending on the biodiesel feedstock type. For the B5 blends tested, B5-SME and B5-WCOME both showed measurable increases in NO_x emissions, while the B5-AFME showed a slight reduction or no change in NO_x emissions compared to the CARB reference diesel fuel. The B5-AFME blend also passed the criteria of the CARB emission equivalent certification test. The results also showed that certain additives can provide some benefits in NO_x reduction, but that the benefits of the additives tested in this study were not sufficient to provide NO_x neutrality at the B20 level. Overall, these additives showed less success than what was seen previously for a 1% DTBP additive blend, which showed NO_x neutrality at the B20 level. Additional testing is currently being planned to more comprehensively investigate the impacts of biodiesel at B5 and B10 levels in CARB diesel. It should also be noted that while the test matrix was fairly robust, it was for only a single engine. So, a wider range of actual results would probably be found over a broader range of engines/vehicles under real-world operating conditions.

From a broader perspective on air quality, the potential for increased NO_x emissions would need to be evaluated in a larger context of potential reductions in other emissions, such as PM, lifecycle analyses for GHGs, and full urban air shed modeling. Previous studies by the National Renewable Energy Laboratory have shown that NO_x increases even for widespread use of B20 level would result in relatively minor impacts in ozone in urban area. For ambient PM, tradeoffs between reductions in primary PM emissions compared to the potential for NO_x to form secondary PM would need to be evaluated. Another important consideration is the expanding use of NO_x control technologies, such as selective catalytic reduction (SCR), since it appears that the impact of biodiesel on NO_x emission increases will largely be eliminated with such devices. As such, in California, the requirements for biodiesel NO_x mitigation are expected to sunset once 95% of the fleet is equipped with NO_x aftertreatment, which is expected to be in 2024. Continuing evaluation of these issues is ongoing in California, where biodiesel penetration into the diesel market is still only about 0.5% of the total fuel volume use. Currently, California is not planning to require biodiesel mitigation until the effective biodiesel blend level, in the marketplace reaches 10%, where the effective blend level would take into consideration other fuels such as renewable diesel that would reduce NO_x emissions. Since the effective biodiesel blend level in the state is not expected to reach 10% until after the 2024 sunset of the biodiesel NO_x mitigation requirement, it is likely that biodiesel NO_x mitigation will not be needed in California [61]. Further study of the potential biodiesel NO_x impacts at B5 and B10 levels is ongoing, however. In Europe, where diesel fuel typically has lower aromatics and higher cetane numbers, greater impacts may be seen, since diesel fuel has a greater share of the transportation market and since biodiesel represents closer to 7% of the overall diesel fuel market. In countries or urban areas using less refined, higher aromatic diesel fuels, there would likely be reduced tendency for NO_x to increase with biodiesel compared with that found in this study, especially at the B5 level.

Disclaimer

The statements and conclusions in this report are those of the contractor and not necessarily those of California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

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Appendix A. Supplementary data

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