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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.

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