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ORIGINAL PAPER

Exhaust Emissions from an Engine Fueled with Biodiesel from High-Oleic Soybeans

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Abstract Biodiesel is a fuel comprising mono-alkyl esters of medium to long-chain fatty acids derived from vegetable oils or animal fats. Typically, engines operated on soybean-based biodiesel exhibit higher emissions of oxides of nitrogen (NOx) compared with petroleum diesel. The increase in NOx emissions might be an inherent characteristic of soybean oil's polyunsaturation, because the level of saturation is known to affect the biodiesel's cetane number, which can affect NOx. A feedstock that is mostly monounsaturated (i.e. oleate) helps to balance the tradeoff between cold flow and oxidative stability. Genetic modification has produced a soybean event, designated 335-13, with a fatty acid profile high in oleic acid (>85%) and with reduced palmitic acid (<4%). This high-oleic soybean oil was converted to biodiesel and run in a John Deere 4045T 4.5-L four-stroke, four-cylinder, turbocharged direct-injection diesel engine. The exhaust emissions were compared with those from conventional soybean oil biodiesel and commercial No. 2 diesel fuel. There was a significant reduction in NOx emissions ($\alpha = 0.05$) using the high-oleic soybean biodiesel compared with regular soybean oil biodiesel. No significant differences were found between the regular and high-oleic biodiesel for unburned hydrocarbon and smoke emissions.

Keywords Genetically modified soybean · High-oleic soybean · Alkyl esters · Biodiesel · Diesel fuel · Diesel engine · Diesel combustion · Diesel emission · NOx emission

Introduction

The search for energy independence and concern for a cleaner environment have generated significant interest in biodiesel, despite its shortcomings. These shortcomings include increased NOx emissions in the engine exhaust, poorer cold-flow properties, and shorter shelf life compared with petroleum diesel. New exhaust emissions technologies may alleviate the NOx problem of biodiesel. The NOx emissions are of interest in this work from a fuel perspective. High-oleic soy methyl esters (HOME) were investigated to see if the NOx emissions can be reduced compared with normal soy methyl esters (SME) and No. 2 diesel fuel.

Biodiesel, a renewable alternative to diesel fuel, is oxygenated, biodegradable, non-toxic, and environmentally friendly. Biodiesel consists of the alkyl monoesters of fatty acids from triacylglycerols (TAG), and it can be produced from vegetable oils, animal fats, and waste restaurant grease. It is miscible with petroleum diesel and the resulting biodiesel–diesel blends are denoted BXX, where

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XX is the percent of biodiesel in the blend. So, B20 is 20% biodiesel in a diesel–biodiesel blend, and B100 is a neat biodiesel fuel.

The fuel properties of biodiesel, for example cetane number, oxidative stability, cloud point, pour point, viscosity, density, and heating value are directly related to the fatty acid (FA) profile of the original source material. These relationships can be used for combustion modeling [1–3]. The individual properties of the alkyl esters will affect the final biodiesel fuel properties [4]. Thus, the properties of biodiesel can be altered by careful feedstock selection, or by modification of the feedstock to obtain a desired FA profile. This work focused on the effect of a high-oleic feedstock on NOx emissions.

In soybean seeds, oleic acid is typically converted to linoleic acid in a single step catalyzed by Δ12 desaturase activity encoded primarily by the FAD2-1 gene [5]. Down-regulation of this gene results in the accumulation of oleic acid in seed storage lipids to approximately 80% [6, 7]. The FatB gene encodes for a palmitoyl-ACP thioesterase [8]. Down-regulation of this gene reduces the accumulation of palmitic acid. Buhr et al. [7] described the simultaneous down-regulation of FatB and FAD2-1, in a seed-specific fashion in soybean. This work resulted in the identification of a soybean event designated 335-13 that has a fatty acid profile high in oleic acid (>85%) with reduced palmitic acid (<4%).

Szybist et al. [9] investigated the effects of reduced iodine value and increased cetane number on a variety of fuels. The fuels were doped with methyl oleate and 2-ethylhexyl nitrate (2-EHN) to study these effects. A total of five fuels were tested: ultra low sulfur diesel (ULSD), a B20 blend of soy biodiesel and ULSD, a B20 blend consisting of mid-oleic (44.5%) soy biodiesel, a B20 blend consisting of high-oleic (76.4%) biodiesel, and a B20 containing 1,000 ppm 2-EHN and pure soy biodiesel. It was found that in all cases the derived cetane numbers (ASTM D6890-03a) were in good agreement with the ignition delays of the samples measured in the engine. They concluded that NOx emissions were insensitive to the rate of heat release and maximum cylinder temperature, but were sensitive to the timing of the maximum cylinder temperature. Interestingly, the B20 blend with high methyl oleate concentration produced NOx emissions that were not significantly different from those from the ULSD fuel.

The objective of the engine testing was to compare the exhaust emissions of the high-oleic (>85%) soybean oil biodiesel (B100) with standard conventional soybean oil biodiesel (B100) and commercial No. 2 diesel fuel.

Experimental Procedures

High-oleic soybeans were obtained from the soybean biotechnology program of the University of Nebraska-Lincoln (Lincoln, NE, USA). Conventional soybeans were obtained from a commercial supplier in Ames, IA, USA. The oil from each type of soybean was extracted and the methyl esters of both soybean oils were produced in a biodiesel pilot plant, which is part of the Iowa Energy Center's Biomass Energy Conversion Center (Nevada, IA, USA).

The fatty acid profiles of the standard soybean oil and the high-oleic soybean oil are given in Table 1. Table 1 includes two different high-oleic soybean oil profiles based on different shipments from separate growing seasons. The engine tests were conducted with the first shipment, but some fuel property measurements, for example cetane number and cold-flow properties, were carried out with fuel produced from the second shipment. The fatty acid profiles of the two shipments are similar with both having about 85% oleic acid. The fuel properties of the three test fuels are given in Table 2.

Exhaust emission tests were conducted in the Internal Combustion Engine Laboratory of Iowa State University. A 2001 (Tier 1) John Deere 4045T (4.5-L, four-cylinder, four-stroke, turbocharged diesel engine) was used for characterization of the exhaust emissions. This engine was coupled to a General Electric DC dynamometer (TLC 2524). No. 2 diesel fuel was included in the testing as a baseline to characterize the emissions from high-oleic methyl esters (HOME) biodiesel, and conventional soy methyl esters (SME). A more detailed description of the test procedures and the equipment setup can be found elsewhere [10, 11].

Triplicate measurements were made of carbon monoxide (CO), carbon dioxide (CO_2), unburned hydrocarbons

Table 1 Fatty acid profiles for both soy biodiesel fuels

Fatty acid profile	Soy methyl esters (SME)[a]	High-oleic methyl esters (HOME)[a], from 1st shipment	High-oleic methyl esters (HOME)[b], from 2nd shipment
C16:0 hexadecanoic (palmitic)	10.81	4.07	3.4
C18:0 octadecanoic (stearic)	4.54	2.73	2.9
C18:1 octadecenoic (oleic)	24.96	85.0	85.3
C18:2 octadecadienoic (linoleic)	50.66	4.28	2.6
Others	8.7	3.9	5.8

[a] Measured at Eurofins Laboratories (Des Moines, IA, USA)

[b] Measured at the University of Idaho (Moscow, ID, USA)

Table 2 The physical and chemical properties of No. 2 diesel fuel, and both soy methyl esters

Test property	No. 2 diesel fuel	Soy methyl ester (SME)	High-oleic methyl ester (HOME)**
Carbon (% mass)[d]	86.66[a]	77.00	77.00
Hydrogen (% mass)[d]	12.98[a]	12.18	12.20
Oxygen (% mass)[d]	–	10.82	10.80
C/H Ratio	6.676	6.322	6.322
Sulfur (% mass)[a]	0.034	<0.005	<0.005
Typical formula	$C_{14.01}H_{25.00}$[b]	$C_{18.74}H_{34.51}O_2$[d]	$C_{18.92}H_{35.73}O_2$[d]
Average molecular weight	194.14[b]	291.73[d]	295.25[d]
Cetane number (ASTM D613)[a]	42.2	50.4	51.5
Hydrocarbon type, FIA (ASTM D1319)[a]			
Saturates	56.6	–	–
Olefins	1.6	–	–
Aromatics	41.8	–	–
Gross heat of combustion (Btu/lb)[a]	19,419	17,183	17,267
Net heat of combustion (Btu/lb)[a]	18,235	16,072	16,208
Specific gravity[c]	0.8559	0.8796	0.8750
Kinematic viscosity (at 40°C; mm^2 s^{-1})[c]	2.8911	4.5926	4.87
Total glycerol (%)[c]	–	0.175	0.068
Cloud point (°C)	−18	1	−5
Pour point (°C)	−30	0	−9

** Values obtained from the second shipment of high-oleic soybeans and measured at the University of Idaho, unless stated otherwise

[a] Measured by Phoenix Chemical Laboratory, Chicago, IL, USA

[b] Calculated using universal oil products method 375-86, available at http://www.astm.org

[c] Measured at the Mechanical Engineering Department, Iowa State University

[d] Calculated from fatty acid profile unless stated otherwise

(HC), oxides of nitrogen (NOx), and Bosch smoke number. The engine emissions are reported on a brake-specific (BS) basis (g kW^{-1} h^{-1}) for a steady-state operating condition of 352.5 N m and 1,400 rpm, which corresponds to peak torque for the engine. Analysis of variance (ANOVA) was performed on the data to determine whether there were significant differences between any two fuels. Post hoc testing was done using the Tukey method to determine whether there were any significant differences between the means of all possible pairs.

Results and Discussion

The reduced saturation and polyunsaturation of the high-oleic soybean oil is its most distinguishing characteristic shown in Table 1, with both the palmitic and linoleic acid content reported at a 3–4% level. For reference, soybean oil usually has approximately 10% palmitic acid and over 50% linoleic acid. The reduced saturation causes a considerable improvement in the cold-flow properties of HOME, which is in agreement with previous fundamental work [12]. The cloud point and pour points of HOME were measured to be −5 and −9°C, respectively. Typical soy biodiesel has cloud and pour points of 1 and 0°C, respectively. The cold-flow properties of the HOME resemble those of low-palmitic soy, which is reported to have a cloud point of −7°C and a pour point of −9°C [13], but the HOME has the added advantage of increased oxidative stability, because of its low polyunsaturation level. Previously, it was demonstrated that methyl linoleate and methyl linolenate oxidized 12 and 25 times faster, respectively, than methyl oleate [14].

The various brake-specific emission results are given in Fig. 1. The letters above the bars indicate whether the mean values are different statistically. For example, if the three bars share the same letter the means are not significantly different. The error bars indicate the minimum and the maximum values of triplicate measurements. The BSNOx emissions of SME and HOME were 13.5 and 7.5% higher than for No. 2 diesel fuel. These increases were statistically significant, and from the post hoc Tukey test, the decrease in BSNOx emissions of the HOME compared with SME was also significant (α = 0.05).

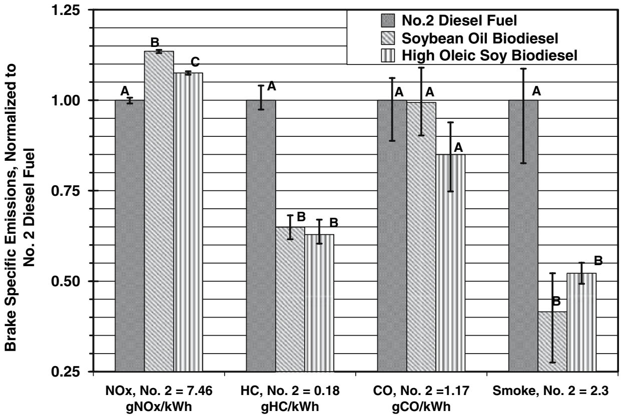

Fig. 1 Brake-specific emission comparisons of No. 2 diesel, standard soybean, and high-oleic soybean biodiesel

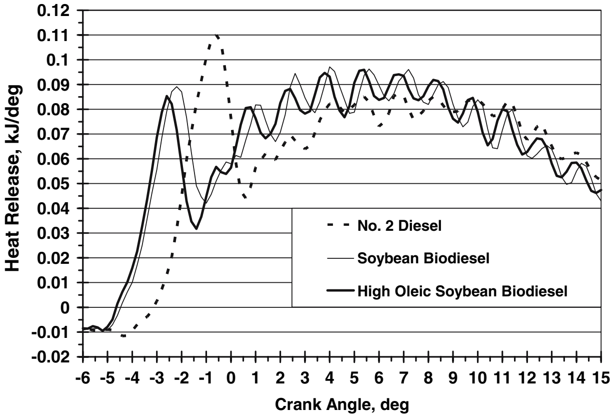

Fig. 2 Heat release analysis for No. 2 diesel, standard soybean biodiesel, and high-oleic soybean biodiesel

This result confirms previous work by McCormick et al. [15] in which an increase in unsaturation led to higher NOx emissions. The relative increase in NOx emissions for the HOME compared with diesel fuel is also in agreement with results from a newer engine [16]. Knothe et al. [16] reported a 6% increase (relative to diesel fuel) when fueling a 2003 Detroit Diesel Corporation 60 series engine with technical grade methyl oleate.

The brake-specific HC and Bosch Smoke Number emissions of the two biodiesel fuels were lower by 35 and 50%, relative to No. 2 diesel fuel. There was no significant difference among BSCO emissions for the three fuels. With the exception of the BSNOx emissions, the two biodiesel fuels were not significantly different from each other for the pollutants reported here.

The start of injection, start of combustion, and ignition-delay time are shown in Table 3, with the standard deviations in parentheses. The ignition delay is the elapsed time between the start of fuel injection and the start of combustion, as determined from the first rise in the heat release rate. The isentropic bulk modulus and the other physical properties of biodiesel can advance the injection timing by as much as 1° to 2° in comparison with diesel fuel [17, 18]. This effect is particularly pronounced in a pump-line-nozzle injection system. In this work, the difference in the start of injection time between No. 2 diesel fuel and the biodiesel fuels was statistically significant ($p < 0.05$), but HOME and SME were similar. This is not surprising given that the difference between the isentropic bulk modulus for the two biodiesel fuels is small compared with diesel fuel. For perspective, at 40°C, the isentropic bulk modulus of methyl oleate, methyl linoleate, and *n*-octadecane are 1,552.3, 1,590.7, and 1,322.5 MPa, respectively [17, 18].

The average ignition-delay times of No. 2 diesel, SME, and HOME were 3.97, 3.26, and 3.14 crank degrees, respectively, and the differences were significant ($p < 0.05$). The shorter ignition delay of the HOME is evident in the heat-release diagram (averaged) shown in Fig. 2, where it has a lower initial peak and is slightly advanced in timing compared to the SME. The timings for the start of combustion were advanced 1.50° and 1.35° for the HOME and the SME in comparison to No. 2 diesel fuel. This could partially explain the higher BSNOx emissions of the biodiesel fuel samples, where the advance in combustion events could lead to higher peak cylinder temperatures. In diesel engines, the formation of NOx is primarily because of the thermal mechanism arising from high temperatures [19]. Biodiesel produces less soot than diesel fuel, which may lead to increased NOx emissions. The soot acts as a radiative sink and transfers heat from the flame front, which lowers actual cylinder temperatures. This radiative cooling may reduce NOx emissions in the range 12–25% [20]. Combustion simulations using yellow grease methyl esters and soy methyl esters resulted an increase in overall cylinder temperature compared with petroleum diesel [3].

Table 3 Start of injection, start of combustion, and ignition-delay time for No. 2 diesel, standard soybean biodiesel, and high-oleic soybean biodiesel

	Start of injection (crank angle, degrees before top dead center)	Start of combustion (crank angle, degrees before top dead center)	Ignition delay (crank angle, degrees)
No. 2 diesel	−7.09 (±0.08)	−3.11 (±0.07)	3.97 (±0.03)
Soybean biodiesel	−7.72 (±0.06)	−4.46 (±0.10)	3.26 (±0.04)
High-oleic soybean biodiesel	−7.78 (±0.02)	−4.64 (±0.04)	3.14 (±0.02)

It is also clear from Fig. 2 that the premixed combustion phase of the biodiesel fuel samples (<180 J) is lower than for No. 2 diesel fuel (225.6 J), because of the shorter ignition-delay times for the biodiesel fuel samples. Even though the HOME had a slightly advanced start of combustion timing, it had a smaller premixed phase of combustion (147.1 J) than the SME (172.2 J). These differences are statistically significant ($\alpha = 0.05$) and may explain the reduction in BSNOx emissions of the HOME relative to the SME. The shorter ignition-delay time of the HOME can be attributed to its higher cetane number, a result of methyl oleate being the major constituent, instead of methyl linoleate. For comparison, reported values for the cetane number for methyl oleate vary from 55 to 59.3, and those for methyl linoleate vary from 42.2 to 38.2 [4].

High-oleic soybean oil seems to be a better feedstock than normal soy oil for biodiesel production. The tradeoff between cold flow and oxidative stability was moderated by its high monounsaturated content. The HOME had better cold-flow properties, and lower NOx emissions compared with the SME. These results can be extended to biodiesel produced from other high-oleic feedstocks, for example high-oleic safflower or high-oleic canola oils.

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