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Exhaust emissions and fuel properties of partially hydrogenated soybean oil methyl esters blended with ultra low sulfur diesel fuel ☆

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ABSTRACT

Important fuel properties and emission characteristics of blends (20 vol.%) of soybean oil methyl esters (SME) and partially hydrogenated SME (PHSME) in ultra low sulfur diesel fuel (ULSD) were determined and compared with neat ULSD. The following changes were observed for B20 blends of SME and PHSME versus neat ULSD: improved lubricity, higher kinematic viscosity and cetane number, lower sulfur content, and inferior low-temperature properties and oxidative stability. With respect to exhaust emissions, B20 blends of PHSME and SME exhibited lower PM and CO emissions in comparison to those of neat ULSD. The PHSME blend also showed a significant reduction in THC emissions. Both SME and PHSME B20 blends yielded small increases in NO_x emissions. The reduction in double bond content of PHSME did not result in a statistically significant difference in NO_x emissions versus SME at the B20 blend level. The test engine consumed a greater amount of fuel operating on the SME and PHSME blends than on neat ULSD, but the increase was smaller for the PHSME blend.

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1. Introduction

Biodiesel, an alternative fuel composed of mono-alkyl esters of long-chain fatty acids prepared from renewable vegetable oils or animal fats, has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petrodiesel). Biodiesel possesses significant technical advantages over petrodiesel, such as derivation from a renewable and domestic feedstock, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, and superior flash point and biodegradability, as well as reductions in most exhaust emissions. Important disadvantages of biodiesel include inferior oxidative and storage stability and low-temperature operability, lower volumetric energy content, and, in some cases, higher oxides of nitrogen (NO_x) exhaust emissions [1–3]. Although biodiesel can be used in modern unmodified compression–ignition (diesel) engines in neat form, it is more commonly encountered as a blend component in petrodiesel, such as B20 (20% biodiesel by volume in petrodiesel). Currently, blends of up to B5 are allowed by ASTM D975 [4], the U.S. diesel fuel standard (Table 1). In addition, a new ASTM standard, ASTM D7467 [5] (Table 1), was recently adopted for blends from B6 to B20 in petrodiesel. Biodiesel must be certified as acceptable according to ASTM D6751 [6], the B100 standard (Table 1), before it can be used as a blend component in petrodiesel per either ASTM D975 or D7467.

Exhaust emissions regulated by title 40, part 86 of the U.S. Code of Federal Regulations include NO_x, particulate matter (PM), total hydrocarbons (THC), and carbon monoxide (CO). Previous studies have confirmed that combustion of B100 in diesel engines results in an average increase in NO_x exhaust emissions of 12% and decreases in PM, THC, and CO emissions of 48, 77, and 48%, respectively, versus petrodiesel [7–12]. For B20 soybean oil methyl ester (SME) blends, NO_x emissions are increased by 0–4% in comparison to petrodiesel, but PM, THC, and CO emissions are reduced by 10, 20, and 11%, respectively [11,12]. This increase in NO_x emissions is of particular concern for environmentally sensitive locations such as national parks and places prone to high levels of air pollution such as urban areas. For biodiesel to be universally accepted, it is desirable to reduce smog-forming NO_x exhaust emissions to levels equal to or lower than those observed for petrodiesel.

The Zeldovich (thermal) and Fenimore (prompt) mechanisms are two potential pathways by which NO_x may be produced during combustion of fuels [10,13–15]. Thermal NO_x is formed at high temperatures when molecular oxygen (O_2) combines with molecular nitrogen (N_2). Prompt NO_x is produced by a complex pathway whereby hydrocarbon radicals react with N_2 to form species that subsequently react with O_2 to form NO_x. However, a previous study concluded that there is negligible NO_x production by the prompt mechanism during combustion of petrodiesel [16]. Consequently, the

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Table 1
Selected specifications from biodiesel and ULSD fuel standards.

	Biodiesel		ULSD	Biodiesel blends
	ASTM D6751	EN 14214	ASTM D975	ASTM D7467
% (vol) biodiesel	100	100	0–5	6–20
Sulfur, max	15 ppm	10 mg/kg	15 ppm	15 ppm
CP, °C	Report		Guidance[a]	Guidance[a]
PP, °C			Guidance[a]	Guidance[a]
CFPP, °C		Variable[b]	Guidance[a]	Guidance[a]
IP, 110 °C, h	3 min	6 min		6 min
υ, 40 °C, mm^2/s	1.9–6.0	3.5–5.0	1.9–4.1	1.9–4.1
Lub, 60 °C, µm			520 max	520 max
AV, mg KOH/g	0.50 max	0.50 max		0.30 max
Cetane number	47 min	51 min	40 min	40 min
IV		120 max		

[a] ASTM D975 and D7467 contain guidance for low-temperature operability, but no requirements.
[b] Depends on location and time of year.

Zeldovich pathway is believed to be the dominant mechanism responsible for NO_x exhaust emissions during combustion of petrodiesel [16,17] and biodiesel [14,18]. A third mechanism largely irrelevant to biodiesel is that of fuel NO_x [14], which is formed when nitrogen that is chemically bound to the fuel combines with excess O_2 during combustion. Biodiesel does not normally contain nitrogen, so NO_x formation by the fuel NO_x mechanism can be considered negligible.

It is well documented that higher cetane numbers (CN) tend to reduce NO_x emissions among fuels of similar type [15,18–20]. Cetane number is influenced by the chemical nature of the fatty acid methyl esters (FAME) that constitute biodiesel. Specifically, a previous study demonstrated that decreasing the chain length and/or increasing the number of double bonds (i.e., higher iodine value (IV)) of FAME resulted in a decrease in CN [21]. Correspondingly, previous studies have shown that decreasing the chain length and/or increasing the number of double bonds (i.e., higher IV) of FAME results in an increase in NO_x emissions [22–24]. The chemical composition of biodiesel varies according to the feedstock from which it is prepared. As a result, biodiesel obtained from feedstocks of significantly different composition exhibit different NO_x exhaust emissions behavior, as evidenced by a comparison of beef tallow methyl esters (IV 54; +0.0% increase in NO_x over petrodiesel), lard methyl esters (IV 63; +3.0%), chicken fat methyl esters (IV 77; +2.4%), and SME (IV 129; +6.2%) [25]. Enrichment of SME with up to 76% methyl oleate (methyl 9(Z)-octadecenoate) resulted in the elimination of the increase in NO_x emissions of B20 blends [26]. Other studies have confirmed the influence of differing FAME compositions on NO_x emissions of B100 and blends with petrodiesel [27,28].

In previous work [29] we described the production of partially hydrogenated SME (PHSME) and the determination of its properties relative to ASTM D6751 [6] and EN 14214 [30], the accepted US and European fuel standards for biodiesel, respectively. Partial hydrogenation of soybean oil was of particular interest as a result of the IV requirement (120 maximum) contained within EN 14214. Soybean oil methyl esters normally do not satisfy the IV requirement in EN 14214, as it typically has IV in the range of 120–135 [29]. In an effort to ensure that soybean oil-derived biodiesel has adequate access to all major world biodiesel markets, we lowered the IV of SME through chemical means. Because the oleochemical industry has significant expertise with catalytic partial hydrogenation of vegetable oils, we chose this method in our previous work to chemically modify soybean oil-based biodiesel to satisfy the IV requirement found in EN 14214.

The objective of the current study was to compare the regulated exhaust emissions of B20 blends of SME (IV 134) and partially hydrogenated SME (PHSME, IV 116) to ultra low sulfur diesel fuel (ULSD, <15 ppm S) using a 2002 Cummins ISB diesel engine. Also of interest was a comparison of ULSD, B20 SME, and B20 PHSME for important fuel properties, such as low-temperature operability, cetane number, sulfur content, oxidative stability, lubricity, acid value, and kinematic viscosity. The PHSME was of interest because it is derived from a plentiful vegetable oil feedstock; soybean oil ranked second in annual worldwide production in 2008 according to the U.S. Department of Agriculture [31]. In addition, PHSME is satisfactory according to the European biodiesel standard, EN 14214 [30], with regard to IV (<120) and oxidative stability (>6 h, according to EN 14112 [32]) whereas untreated SME cannot satisfy the IV requirement. Also, because of the higher level of allylic methylene positions in SME, it is less stable to oxidation than PHSME according to the Rancimat (EN 14112) method [29].

2. Experimental section

2.1. Reagents and materials

The baseline diesel fuel was a 2007 Certification ULSD supplied by Haltermann Products (Channelview, Texas, USA) that was used for baseline comparison as well as the petrodiesel blend stock for the biodiesel blends. Soybean oil methyl esters (IV 134; measured according to American Oil Chemists' Society (AOCS) official method Cd 1c-85) were supplied by Agland, Inc. (Eaton, Colorado, USA). Partially hydrogenated soybean oil (PHSBO, IV 116) was donated by the Oils & Fats division of Archer Daniels Midland Company (Decatur, Illinois, USA). All other chemicals and reagents were obtained from Aldrich Chemical Company (Milwaukee, Wisconsin, USA) and used as received. The SME and PHSME (their preparation is described in Section 2.2) were blended at 20% by volume into the baseline 2007 Certification ULSD fuel.

2.2. Methanolysis of partially hydrogenated soybean oil

Methanolysis of PHSBO was accomplished as described in a previous work [29] with a sodium methoxide catalyst (0.5 wt.% with respect to PHSBO), 6:1 molar ratio of methanol to PHSBO, 60 °C internal reaction temperature, and 1.5 h reaction time. After the glycerol was removed by gravity separation, the crude methyl esters were washed with distilled water until a neutral pH was obtained. The ester phase was then dried by treatment with anhydrous magnesium sulfate ($MgSO_4$) to afford PHSME, which was independently verified as satisfactory according to ASTM D6751 by Magellan Midstream Partners, L.P. (Kansas City, Kansas, USA).

2.3. Fuel properties of ULSD and B20 samples

All measurements were made in triplicate except where indicated and mean values are reported (Table 2). Cloud (CP, °C) and pour points (PP, °C) were measured in accordance to ASTM D5773 and D5949, respectively, using a model PSA-70S Phase Technology Analyzer (Richmond, B.C., Canada). CP and PP were rounded to the nearest whole degree (°C). For a greater degree of accuracy, PP measurements

Table 2
Fuel properties of ULSD and B20 SME and PHSME.

Property	ULSD	B20 SME	B20 PHSME
CP, °C	-20 ± 1	-15 ± 1	-14 ± 1
PP, °C	-24 ± 1	-22 ± 1	-19 ± 1
CFPP, °C	-20 ± 1	-17 ± 1	-17 ± 1
IP, 110 °C, h	28.9 ± 0.9	3.2 ± 0.2	9.0 ± 0.1
υ, 40 °C, mm^2/s	2.67 ± 0.01	2.84 ± 0.01	2.94 ± 0.01
Lub, 60 °C, µm	538 ± 5	182 ± 3	197 ± 3
DCN[a]	41.4	45.1	47.3
Sulfur, ppm	10	8	8
AV, mg KOH/g	0.00	0.08 ± 0.03	0.05 ± 0.03

[a] Derived cetane number.