

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231270658>

Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstock: A High Quality Renewable Fuel Produced from a Waste Feedstock||

ARTICLE *in* ENERGY & FUELS · JUNE 2001

Impact Factor: 2.79 · DOI: 10.1021/ef010051x

CITATIONS

142

READS

287

4 AUTHORS, INCLUDING:



[Karen Michele Wagner](#)

United States Department of Agriculture

23 PUBLICATIONS 836 CITATIONS

SEE PROFILE



[T. L. Alleman](#)

National Renewable Energy Laboratory

46 PUBLICATIONS 932 CITATIONS

SEE PROFILE



[Robert L McCormick](#)

National Renewable Energy Laboratory

157 PUBLICATIONS 3,880 CITATIONS

SEE PROFILE

Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstock: A High Quality Renewable Fuel Produced from a Waste Feedstock^{II}

Michael J. Haas,^{*,†} Karen M. Scott,[†] Teresa L. Alleman,^{‡,§} and Robert L. McCormick^{‡,§}

U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, Pennsylvania 19038, and Colorado Institute for Fuels and Engine Research, Colorado School of Mines, Golden, Colorado 80401

Received February 28, 2001. Revised Manuscript Received May 30, 2001

A previously developed bench-scale method for the production of fatty acid methyl esters (biodiesel) from soybean soapstock (Haas, M. J.; Bloomer, S.; Scott, K. *J. Am. Oil Chem. Soc.* **2000**, *77*, 373–379) was taken to the small pilot scale, producing approximately 2.5 L of material per run. By multiple successive reactions, 25 L of product was accumulated. The fatty acid composition of the ester product (wt %) was palmitic: 16.2, stearic: 4.7, oleic: 16.2, linoleic: 54.4, and linolenic: 6.9. This mirrors the fatty acid composition of soy soapstock and is quite similar to that of commercial biodiesel produced from refined soybean oil. The ester product met the provisional biodiesel specifications of the American Society for Testing and Materials with regard to all variables examined: flash point, water and sediment, carbon residue, sulfated ash, density, kinematic viscosity, sulfur, cetane number, cloud point, copper corrosion, acid number, free glycerin, and total glycerin, and had density and iodine number values comparable to those of commercial soy-based biodiesel. Emissions data for both the neat fuel and a 20 vol % blend in low-sulfur petroleum diesel were collected according to the Environmental Protection Agency heavy-duty transient cycle protocol using a DDC Series 60 engine on an engine test stand. The emissions profile of biodiesel from soapstock was quite similar to that of biodiesel produced from refined soy oil. Compared with petroleum diesel fuel, emissions of total hydrocarbons, particulates, and carbon monoxide were reduced 55%, 53%, and 48%, respectively, with neat soapstock biodiesel. Total nitrogen oxides increased 9%. Operation on a 20 vol % blend of soapstock biodiesel in petroleum diesel gave reductions of 27.7%, 19.7%, and 2.4%, respectively, in total hydrocarbons, particulate matter, and carbon monoxide, relative to petroleum diesel. Nitrogen oxide emissions increased 1.3%. In the context of engine emissions, these data suggest the suitability of the methyl esters of soy soapstock as a diesel fuel.

Introduction

Oxygenated fuels have a history of reducing exhaust emissions from motor vehicles. Additions of methyl tertiary butyl ether and ethanol have shown success in reducing emissions from gasoline engines. In high-polluting spark-ignition engines, oxygenated gasoline can decrease carbon monoxide (CO) from automobiles. Oxygenates are now mandated by the U.S. Clean Air Act for use in reformulated and CO control gasoline. This success of oxygenated gasoline has sparked interest in the use of oxygenated compounds as emissions-reducing additives in fuel for compression ignition (diesel) engines. Oxygenated compounds used as diesel

additives are structurally similar to diesel fuel but have one or more oxygen atoms bonded to the hydrocarbon chain. Oxygenated fuels are also of special interest because in many cases they are components of, or can be produced from, agricultural products, and thus have potential as domestically produced and renewable sources of energy. Here we describe the production and utilization of a form of oxygenated diesel fuel known as biodiesel, from soapstock, a byproduct of vegetable oil processing.

Biodiesel is the name given to the monoalkyl esters of animal- or vegetable-derived long chain fatty acids when intended for use as replacements for petroleum-derived fuel in diesel engines. Extensive research conducted worldwide,^{1–3} especially in the past two decades, has resulted in the development and optimiza-

* Author to whom correspondence should be addressed, at USDA, ARS, ERRC, 600 East Mermaid Lane, Wyndmoor, PA 19038. Tel: U.S. 215-233-6459. Fax: U.S. 215-233-6795. E-mail: mhaas@arserrc.gov.

[†] U.S. Department of Agriculture, Agricultural Research Service.

[‡] Colorado Institute for Fuels and Engine Research, Colorado School of Mines.

[§] Present address: National Renewable Energy Laboratory, Golden, CO 80401.

^{II} Mention of brand or firm names does not imply endorsement by the U.S. Department of Agriculture over others of similar performance not mentioned.

(1) Tyson, K. S. National Renewable Energy Laboratory, Report No. NREL/SR-580-24433, Golden, CO, 1998.

(2) *Biodiesel: A Technology, Performance, and Regulatory Overview*, National SoyDiesel Development Board, Jefferson City, MO, 1994.

(3) Sheehan, J.; Camobreco, V.; Duffield, J.; Graboski, M.; Shapouri, H. National Renewable Energy Laboratory, Report No. NREL/SR-580-24089, Golden, CO, 1998.

tion of methods for the synthesis of biodiesel from a variety of lipids via chemical or enzymatic catalysis,⁴ the conduct of engine performance evaluations in static and mobile configurations, characterization of the emissions of engines fueled with biodiesel,⁵ and investigation of the toxicity of these emissions. These studies have established the suitability of biodiesel from a performance standpoint, its attractiveness relative to petroleum-derived diesel in terms of enhanced fuel lubricity, reduced emission of regulated air pollutants, and reduced toxicity for those pollutants that are emitted. Hundreds of hours of static engine tests and millions of miles of road tests have been conducted with biodiesel-fueled engines,^{1,5} and the technology is presently entering the commercial marketplace in the United States.

A number of prior studies examined the emission of regulated air pollutants from engines fueled with biodiesel and with blends of biodiesel and petroleum-derived diesel fuel. Graboski and McCormick⁵ reviewed many of these studies. It is typically observed that biodiesel reduces emissions of CO, hydrocarbons (HC), mutagens, air toxics and particulate matter (PM), or soot, relative to petroleum diesel, but slightly increases levels of oxides of nitrogen (NO and NO₂, collectively termed NO_x). For example, Graboski and co-workers⁶ tested methyl soyester neat and in blend, with petroleum diesel in a 1991 Detroit Diesel Series 60 (4-stroke) truck engine. For B-35 (that blend of fuels consisting of 35 vol % biodiesel in petroleum diesel) composite NO_x emission increased by nearly 1%, while composite PM emission decreased 26% relative to the reference diesel. For B-100 (neat biodiesel), composite NO_x increased by 11% while PM decreased by 66%. The extent of PM reduction appears to depend in part on the fuel injection technology of the engine tested, and other factors. Emissions also depend on biodiesel chemical composition, and are thus feedstock-dependent. Determination of the emissions profile is a key step in assessing the acceptability of a biodiesel fuel produced from a new feedstock.

A major bottleneck to the adoption of biodiesel as a fuel has been its cost. Initially, refined oils, especially soybean oil in the United States and rapeseed oil in Europe, were the most common feedstocks for biodiesel production. The average cost of refined soybean oil in the United States between 1993 and 1995 was \$2.00/gal, and it has been estimated that its conversion to biodiesel adds a net additional cost of \$0.52/gal.⁷ In contrast, the U.S. average refiner price of petroleum diesel to end users was \$0.57/gal between 1993 and 1995.⁷ As a result of its relatively high cost, biodiesel made from refined soy oil could have difficulty competing economically with petroleum-derived diesel fuel.^{7,8} Realization of this fact has stimulated investigation of the suitability of lower value lipids, primarily animal

fats and waste greases, as feedstocks for biodiesel production.^{4, 9–11}

Vegetable oil refining generates a relatively inexpensive byproduct, known as soapstock (SS), that is rich in the fatty acids that are the precursors of biodiesel. Soapstock consists largely of water, acylglycerides, phosphoglycerides, and free fatty acids. The total fatty acid content, including both free- and lipid-linked acids, is 25–30% (weight basis). Annual U.S. production of SS from soybeans, the predominant oilseed processed in this country, is approximately one billion pounds. Lesser amounts are also produced during the processing of other oilseeds. The price of SS can be as low as one-tenth or less that of refined vegetable oil. We have previously developed and optimized a bench-scale method for the synthesis of fatty acid methyl esters (FAME) from soybean soapstock, and shown that the composition of the product meets the Provisional Standards for Biodiesel proposed by the American Society for Testing and Materials.¹² Since SS differs compositionally from refined triglyceride oils and animal fats, an examination of the engine emissions characteristics of an ester fuel produced from SS is necessary to assess its suitability as a fuel. We have therefore expanded the scale of the synthetic reaction, and conducted an initial determination of the emission properties of the resulting fuel in a typical diesel truck engine using the heavy-duty Federal test procedure.

Materials and Methods

Chemicals. Soybean SS generated by the industrial refining of crude soybean oil with sodium hydroxide was a gift of Cargill Inc., Gainesville, GA. Organic solvents, sulfuric acid (96.3 wt %), sodium hydroxide (50 wt %), and lipid standards for gas chromatography (GC) and high-performance liquid chromatography (HPLC) were obtained as previously described.¹² Methanol for esterification was dried over anhydrous sodium sulfate before use. Calcium oxide (CaO, Codex Hydrated Lime) was obtained from Mississippi Lime Co., Alton, IL.

Fuels. To provide an emissions reference point and control, testing of biodiesel fuels was accompanied by and compared with tests on a conventional (petroleum-derived) diesel. This was certification diesel fuel obtained from Phillips Petroleum (Borger, TX, Lot D434). The properties of this fuel are shown in Table 1. This reference diesel was also used in preparing B-20 blends. In addition to methyl esters of soapstock, a commercial soybean oil methyl ester fuel (Soygold, Ag Environmental Products, Lenexa, KS) was tested because soy oil-based biodiesel is by far the most common biodiesel fuel studied to date.

Synthesis of Fatty Acid Methyl Esters. Esterification of the fatty acids in SS involved the alkaline hydrolysis of all fatty acid ester bonds, followed by water removal and acid-catalyzed methyl esterification.¹²

• Saponification: Soapstock (14 kg) was added to an open 24 L steam-jacketed stainless steel kettle and heated to 100 °C. To this was added 50 wt % sodium hydroxide at a rate between 8% and 12% (wt of sodium hydroxide solution/wt of

(4) Haas, M. J.; Piazza, G. J.; Foglia, T. A. *Lipid Biotechnology*; Kuo, T. M., Gardner, H. W., Eds.; Marcel Dekker: New York, in press.

(5) Graboski, M. S.; McCormick, R. L. *Prog. Energy Combust. Sci.* **1998**, *24*, 125–164.

(6) Graboski, M. S.; Ross, J. D.; McCormick, R. L. *Society of Automotive Engineers*, Paper No. 961166, Warrendale, PA, 1996.

(7) Duffield, J.; Shapouri, H.; Graboski, M.; McCormick, R.; Wilson, R. USDA Economic Research Service, Washington, DC, Agricultural Economic Report No. 770, 1998.

(8) Ahouissoussi, N. B. C.; Wetzstein, M. E. USDA Economic Research Service, Report IUS-5S, 3-9, Washington, DC, 1996.

(9) Mittelbach, M.; Tritthart, P. *J. Am. Oil Chem. Soc.* **1988**, *65*, 1185–1187.

(10) Ali, Y.; Hanna, M. A.; Cuppett, S. L. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1557–1564.

(11) Peterson, C. L. *Commercialization of Biodiesel: Producing a Quality Fuel*; Peterson, C. L., Ed.; University of Idaho, Moscow, ID, 1998; pp 22–31.

(12) Haas, M. J.; Bloomer, S.; Scott, K. *J. Am. Oil Chem. Soc.* **2000**, *77*, 373–379.

Table 1. Properties of Certification Diesel Fuel Lot D-434 Used as Reference in this Study

Property	Lot D-434	ASTM Method
API gravity	36.28	D-287
viscosity, cs 40 °C	2.5	D-445
net BTU/lb	18456	D-3338
cetane number	46.0	D-613
carbon, wt %	86.6	D-5291
hydrogen, wt %	13.4	D-5291
oxygen, wt %	0	D-5291
sulfur, ppm	300	D-2622
IBP, F	353.9	D-86
T50, F	498.7	D-86
T90, F	583.7	D-86
EP, F	646.4	D-86
aromatics, vol %	29.2	D-1319
olefins, vol %	2.0	D-1319
saturates, vol %	68.8	D-1319

SS). Preliminary experiments with each batch of SS identified the amount of sodium hydroxide necessary to obtain complete saponification of the SS. The mixture was heated and held at 85–100 °C for 4 h. A sample (10 g) was then acidified with 6 N HCl and extracted with 12 mL of hexane. The extract was assayed by HPLC on a silica column to determine the contents of residual glycerides, phosphoglycerides, lysophosphoglycerides, and free fatty acids.¹³

- **Drying:** To increase its surface area, saponified SS at 4 °C was passed through a meat grinder with a 0.9 cm diameter pore size plate. This was spread to a thickness of approximately 5 cm on stainless steel pans, and its moisture content reduced to less than 4% in a shelf-type lyophilizer (Model 100-42, American Lyophilizer, Inc., Bridgeport, PA). The dried material was pulverized in a food processor (Pro Food Prep Center, Cuisinart, East Windsor, NJ) to pass through a 1.25 mm mesh screen and stored at –20 °C under nitrogen.

- **Esterification:** Pulverized, dried, saponified SS (5 kg) was mixed into 11.74 L of dry methanol at 4 °C in a 22 L four-necked round-bottom glass flask equipped with a heating mantle, a motor-driven stirring paddle, and a water-cooled condenser. Cold concentrated sulfuric acid was added slowly until a sample of the mixture, diluted 2-fold in water, gave a reading of at least 410 when measured with a pH meter (PHM 82, Radiometer, Copenhagen, Denmark) operating in millivolt mode. The required amount of acid varied between 1.0 and 1.7 L for different batches of SS, due to variations in the initial degrees of alkalinity in the SS. The solution was blanketed with nitrogen and held between 55 and 69 °C while stirring for 2 h. The mixture was then filtered over Whatman #1 paper. The filtrate was centrifuged 20 min at 4600g and the resulting upper layer (crude FAME) retained. FAME trapped in the solid retained by filtration was recovered as a floating layer following resuspension of the solid in 2 volumes of tap water and centrifugation (20 min, 4600g). The crude ester fractions were pooled, washed twice with 28% (v/v) of 5% NaCl in tap water, followed by 28% (v/v) of 11% (wt/v) sodium bicarbonate in tap water. To remove residual free fatty acids, the ester fraction was washed with one-fifth volume of 4.5 M CaO in tap water and centrifuged (20 min, 4600g). This protocol yielded about 2.5 L of methyl ester per 5 kg of dried saponified SS, which was stored under nitrogen in the dark until engine tests. Through successive reactions, 25 L of fatty acid methyl ester was accumulated.

Analytical Methods. To determine the extents of hydrolysis of glyceride and phosphoglyceride fatty acid ester bonds during saponification of SS, samples were acidified with H₂SO₄, dissolved in hexane and in chloroform/methanol (85:15,

v/v), and analyzed by HPLC along with appropriate standards.¹³ The identities and relative proportions of fatty acids in the methyl ester product were determined by GC using a Hewlett-Packard (HP, Wilmington, DE) model 5890 gas chromatograph with a flame-ionization detector, equipped with an HP-Innowax fused-silica capillary column, 30 m × 0.53 mm (internal diameter).¹⁴ FAME assignments were made by comparison with a standard reference mixture of fatty acid methyl esters (Nu-Check Prep, Elysian, MN). Other properties of the final methyl ester product were determined by Williams Laboratory Services (Kansas City, KS).

Emissions Measurement. The test engine was a 1991 calibration, production model truck engine loaned by the Detroit Diesel Corporation. The six cylinder, four stroke engine was nominally rated at 345 bhp (257 kW) at 1800 rpm and was electronically controlled (DDEC-II), direct injected, turbocharged, and intercooled. All transient cycles were generated from an engine map acquired on certification diesel.

The system for emissions measurement of regulated pollutants (total hydrocarbons [HC], CO, NO_x, and PM) met the requirements for heavy-duty engine emissions certification testing.¹⁵ System details have been described previously.¹⁶ The system includes a supply of humidity- and temperature-controlled intake air, and employed a full flow exhaust dilution tunnel. Dilute exhaust mass flow rate was determined using a critical flow venturi. The concentration of gaseous pollutants in the dilute exhaust was determined as follows:^{5,6} HC by continuous flame ionization, CO and CO₂ by separate NDIR analyzers, NO_x by chemiluminescence. Gas mass emissions were determined by background corrected flow compensated integration of the instantaneous mass rates.

Particulate matter was collected on Pallflex T60A20 70 mm filters of a common lot. Particulate matter was sampled through a secondary tunnel, which ensured a filtered gas temperature below 52 °C. Since the PM mass collected was small, especially for the biodiesel samples, even minor differences in filter weight due to water adsorption could potentially impact the determination of particulate mass emission. Particle filter handling and weighing was therefore conducted in a yellow light, constant humidity room held at 9 ± 2 °C dew point, 50% nominal relative humidity, and 22 ± 1 °C. The volatile organic fraction of PM was determined by placing the filters in a vacuum oven at 225 °C, under a vacuum greater than 55 cm Hg, and with a very low flow of purge air. Filters were maintained in the oven for 2.5 to 3.0 h. Volatile organic fraction (VOF) was determined as the difference between the initial and final weights.

A number of additional measures were taken to ensure that the NO_x and PM measurements were both precise and accurate:

- **Emission Gas Standards:** Emission standard gases were ±1% EPA Protocol Standards. Gas standards were not changed during the test program.

- **Carbon Balance:** As a test quality-assurance check, a carbon balance was performed for each transient test. Diesel mass fuel consumption was monitored with a Micromotion DP-25 mass flow sensor and through weighing of the fuel supply tank before and after a test using a load cell. Exhaust carbon was determined from the background-corrected HC, CO, CO₂, and PM emissions data. PM was assumed to be 100% carbon. For this data set carbon balances were within 4%.

- **NO_x Humidity Correction:** Intake air humidity has a large influence on NO_x emissions. Humidity was measured continuously in the conditioned air inlet by two independently calibrated methods: a dew point meter and a polymer mem-

(14) Juneja, V. K.; Foglia, T. A.; Marmer, B. S. *J. Food Prot.* **1998**, 61, 683–687.

(15) United States Code of Federal Regulation, Vol. 40, Part 86, subpart N.

(16) McCormick, R. L.; Ross, J. D.; Graboski, M. S. *Environ. Sci. Technol.* **1997**, 31, 1144–1150.

(13) Haas, M. J.; Scott, K. M. *J. Am. Oil Chem. Soc.* **1996**, 73, 1393–1401.

brane sensor. Furthermore, the intake air was controlled to an 11.7 °C nominal dew point. The NO_x correction factor, calculated as per 40 CFR 1342–94(d)(8)(iii), was very near unity.

The statistical significance of differences in engine emissions when operating on different fuels was assessed by a two-sample t-test assuming equal variances.

Results and Discussion

Production of Biodiesel from Soapstock. The method employed here for FAME synthesis from soapstock involved the hydrolysis of all fatty acyl ester bonds by saponification, followed by removal of water and the subsequent acid-catalyzed esterification of the resulting free fatty acids. The method is simple and efficient, involves readily available and inexpensive reagents, operates at ambient pressure and relatively low temperatures, and is not difficult to conduct.

The soapstock used here was received as multiple shipments (20 L each) from an industrial edible oil refinery over the course of several months. A typical compositional analysis of this material indicated (wet wt basis) 45.1% water, 10.1% triglycerides, 1.8% diglycerides, <2% monoglycerides, 10.0% free fatty acids, 2.7% phosphatidylcholine, 2.2% phosphatidylinositol, and 3.6% phosphatidylethanolamine. The saponification treatment caused essentially complete hydrolysis of the acylester bonds of glycerides and phosphoglycerides in the SS. After this step, triglycerides, partial glycerides, phosphoglycerides, and lysophosphoglycerides were undetectable by HPLC (minimum detection limits: glycerides: <0.04%, phosphoglycerides and lysophosphoglycerides: <0.06%). The esterification reaction was also highly efficient: HPLC analysis of crude post-esterification mixtures indicated that less than 0.5% of the input free fatty acids remained unesterified. Previous investigations demonstrated that such high degrees of esterification could not be achieved if input SS contained more than 4 wt % water.¹² This value was thus chosen as the maximum allowable water content of dried, saponified SS entering the esterification reaction.

FAME recoveries after the water and NaCl washes averaged 96% of theoretical maximum. However, the free fatty acid content of this material was slightly greater than that consistent with an acceptable acid number measurement in biodiesel. Free fatty acid levels were reduced to 0.2–0.4%, resulting in acceptable acid numbers, by washing with aqueous calcium oxide. Losses of FAME in this step were about 10%. Overall process efficiency could be increased by further optimization of these washes to reduce ester loss.

Characterization of Soapstock-Derived Biodiesel. GC analysis indicated that the FAME product consisted predominantly of the methyl esters of five fatty acids: palmitic, stearic, oleic, linoleic, and linolenic (Table 2). This composition is essentially identical to that reported for soybean oil soapstock (Table 2), indicating that the saponification/esterification method employed here is without bias with regard to fatty acid chain length or degree of unsaturation. Table 2 also presents the fatty acid compositions of soybean oil and of the commercial soy oil-based biodiesel employed here as a reference biodiesel fuel. Reflecting differences in

Table 2. Predominant Fatty Acids in Soybean Oil, Soybean Oil Soapstock, and Methyl Esters Produced from Them^a

fatty acid	soybean oil ^b	soybean oil methyl ester ^c	soybean oil soapstock ^d	soybean oil soapstock methyl ester ^e
palmitic (16:0)	11.5	12	17.2	16.4 (16.2)
stearic (18:0)	4.0	4	4.4	4.8 (4.7)
oleic (18:1)	24.5	25	15.7	16.5 (16.2)
linoleic (18:2)	53.0	53	55.6	55.3 (54.4)
linolenic (18:3)	7.0	6	7.1	7.0 (6.9)

^a Expressed as weight percent of the five predominant fatty acids of soybean oil. These comprise greater than 98% of the total fatty acid content of soy. Actual contents, in weight percent, are shown in parentheses. ^b From Fritz, E.; Johnson, R. W. *Raw Materials for Fatty Acids*. In *Fatty Acids in Industry. Processes, Properties, Derivatives, Applications*; Johnson, R. W., Fritz, E., Eds.; Marcel Dekker: New York, 1989; pp 1–20. ^c Soygold commercial biodiesel produced by Ag Environmental Products, Lenexa, KS; compositional analysis by manufacturer. ^d From Beal, R. E. *Feed Additive for Poultry from Soybean Oil Soapstocks*. U.S. Patent 3,916,031, 1975. ^e This work.

the fatty acid contents of the raw materials from which they were made, soapstock methyl ester contained about 50% more palmitic acid than did soy oil-based biodiesel, and a correspondingly lower amount of oleic acid. It is not clear if these differences are sufficient to confer emissions properties greatly different from those of soapstock biodiesel. The other predominant fatty acids in these preparations (oleic, linoleic, linolenic) were present at comparable levels in FAMES produced from soy oil and soapstock.

The FAME produced from soapstock was assayed to determine selected compositional and physical properties, and the results were compared with the provisional standards for biodiesel published by the American Society for Testing and Materials (ASTM) (Table 3). The material was within specifications for all assayed variables. The cetane number was within one unit of that of FAME produced from soy oil. This is as would be expected, given the similarity in fatty acid compositions between the two feedstocks (Table 2). Saturated fatty acid methyl esters, including methyl palmitate, have substantially higher cetane values than unsaturated ones.⁵ Evidently the effects on cetane number of the elevated palmitic acid ester levels in soapstock-derived FAME relative to soy-oil FAME are approximately counteracted by the cetane-lowering impact of its slightly elevated polyunsaturated fatty acid content. The total glycerin parameter is a measure of the combined contents of free glycerol and glycerol bound in residual tri-, di-, and monoglycerides. Its low value for the SS-derived biodiesel is a reflection of the high efficiency of the saponification reaction, which removed glycerides. The low acid number indicates that any residual free fatty acids remaining after esterification were efficiently removed by the lime wash step.

Engine Emissions. Results of engine testing are reported in Table 4. Certification fuel (roughly speaking, industry average diesel fuel) was tested at the beginning and end of the test program to provide a reference for comparison and to test for drift in the emissions measurement system. Results for NO_x, CO, and PM exhibited excellent repeatability and demonstrated that system drift over the testing program was not significant. The 1991 model year engine used for these tests met all emissions standards for that model year.

Table 3. Properties of Fatty Acid Methyl Esters Synthesized from Soy Oil and Soy Soapstock^a

property	assay method (ASTM)	soy oil methyl ester ^b	soapstock methyl ester	biodiesel provisional standard ^c (max. allowed, unless stated)
flash point (°C)	D93	n.d.	169	100 (min)
water and sediment (vol %)	D2709	<0.01	<0.01	0.05
carbon residue (wt %)	D524	n.d.	0.01	0.05
sulfated ash (mass %)	D874	n.d.	0.020	0.020
density (g/cm ³)	D4052	0.8836	0.885	none
kinematic viscosity (cST, @ 40 °C)	D445	4.03	4.302	1.9–6.0
sulfur (wt %)	D2622	n.d.	0.0015	0.05
cetane	D613	52.3	51.3	40 min
iodine no.	D664	121	129	none
cloud point (°C)	D5773	n.d.	6	none
copper corrosion	D130	n.d.	1A	3B
acid number (mg KOH/g)	D664	0.15	0.05	0.80 mg KOH/g
free glycerin (wt %)	Plank ^f	0.007	0.00	0.02
total glycerin (wt %)	Plank ^f	0.223	0.123	0.240

^a Determined by Williams Laboratory Services, Kansas City, KS. ^b Data for Soygold Brand soybean oil methyl ester. ^c American Society for Testing and Materials, Philadelphia, PA. Provisional Standard PS121. ^d Determined in this lab by high-performance liquid chromatography. ^e n.d.: not determined. ^f Method of Plank, C.; Lorbeer, E. *J. Chromatogr. A* **1995**, 697, 461–468.

Table 4. Emissions Testing Results (1991 DDC Series 60 Engine, Heavy-Duty Federal Test Procedure)

emissions, g/bhp-h:	HC	NO _x	CO	PM ^a	VOF ^b	BSFC ^c
fuel						
certification diesel	0.053	4.624	4.605	0.247	0.014	0.408
certification diesel	0.057	4.664	4.445	0.219	0.011	0.378
certification diesel	0.054	4.634	4.769	0.229	0.017	0.407
average	0.055	4.640	4.606	0.232	0.014	0.398
coefficient of variation	3.3%	0.4%	3.5%	6.0%	19.9%	4.3%
soy biodiesel	0.034	5.054	2.967	0.078	0.014	0.469
soy biodiesel	0.029	5.149	2.697	0.060	0.014	0.452
soy biodiesel	0.031	5.153	2.577	0.060	0.013	0.448
average	0.031	5.119	2.747	0.066	0.014	0.456
coefficient of variation	7.5%	1.1%	7.3%	15.7%	5.4%	2.4%
soapstock biodiesel	0.018	5.034	2.370	0.096	0.022	0.460
soapstock biodiesel	0.024	5.106	2.484	0.117	0.027	0.473
average	0.021	5.070	2.427	0.107	0.024	0.467
coefficient of variation	20.9%	1.0%	3.3%	14.2%	13.6%	1.9%
soapstock B-20	0.043	4.697	4.608	0.189	0.019	ND
soapstock B-20	0.031	4.733	4.558	0.186	0.022	0.398
soapstock B-20	0.029	4.712	4.416	0.176	0.025	0.397
average	0.034	4.714	4.527	0.184	0.022	0.397
coefficient of variation	22.6%	0.4%	2.2%	3.9%	13.3%	0.2%
certification diesel	0.040	4.671	4.668	0.220	0.023	0.404
certification diesel	0.030	4.663	4.700	0.228	0.023	0.387
average	0.035	4.667	4.684	0.224	0.023	0.396
coefficient of variation	19.3%	0.1%	0.5%	2.5%	2.0%	3.0%

^a PM = particulate matter. ^b VOF = volatile organic fraction of PM. ^c BSFC = brake specific fuel consumption, g/bhp-h.

Table 4 also reports results for commercially prepared methyl esters of soybean oil, as well as for methyl esters of soapstock. Soy methyl esters exhibited a roughly 10% increase in NO_x emissions and a 70% decrease in PM emissions relative to certification diesel. Both of these changes were significant at a 99% or greater confidence level. These results are in agreement with previous studies conducted on the same engine.^{6,16,17} The decrease in PM emissions is caused by the oxygen content of the biodiesel fuel, which provides oxygen to the fuel-rich zone of the combustng spray, thereby reducing PM formation. The volatile organic fraction (VOF) of PM is primarily made up of engine oil and unburned fuel and is thus unaffected by fuel choice. VOF was 0.017 ± 0.005 g/bhp-h for this engine independent of fuel composition (Table 4). This highlights the fact that the PM reduction caused by the use of biodiesel is a reduction in the soot or carbonaceous fraction.

The cause of the increase in NO_x emissions observed here and in many other studies⁵ is poorly understood, although several hypotheses have been discussed.^{16–18} For biodiesels from a wide range of feedstocks, NO_x emissions can be correlated with either density, cetane number, or iodine number (degree of unsaturation), as all three of these quantities are correlated with each other.¹⁷ Brake-specific fuel consumption (BSFC, in g/bhp-h) for soapstock biodiesel was comparable to that for soy oil biodiesel, consistent with the similar compositions of these fuels. Their BSFC was 18% higher than for petroleum diesel, consistent with the lower energy content of biodiesels per unit mass. Engine fuel economy on a btu or kJ/bhp-h basis is unaffected by biodiesel.⁵

Because the fuel produced from soybean soapstock has a composition very similar to that of soybean oil methyl esters it would be expected to have similar emissions. This was generally observed here (Table 4).

(17) McCormick, R. L.; Graboski, M. S.; Alleman, T. L.; Herring, A. M.; Tyson, K. S. *Environ. Sci. Technol.*, submitted.

(18) Tat, M. E.; Van Gerpen, J. H.; Soyulu, S.; Canakci, M.; Monyen, A.; Wormley, S. *J. Am. Oil Chem. Soc.* **2000**, 77, 285–289.

Relative to certification diesel, use of soapstock biodiesel increased NO_x emissions by 9% and decreased PM by slightly more than 50%. The NO_x emissions from the two biodiesel fuels tested here were not statistically different. Thus we expect these fuels to have very similar values of cetane number, density, and iodine number, as was observed (Table 3). PM emissions were significantly higher for the soapstock methyl ester fuel than for the soy oil fuel ($p = 0.034$) but were well within the range reported for soy-based biodiesels in similar engines.⁵ We have previously shown that for biodiesels with a cetane number above about 45 the PM emission depends only upon the fuel oxygen content and is not effected by other fuel structural parameters (such as number of double bonds). Thus the oxygen content of the soapstock fuel may have been slightly less than that of the soy-based fuel.

As is typical for diesel engines, hydrocarbon emissions were very low during operation on petroleum diesel fuel. Using either soy oil-derived or soapstock-derived biodiesels gave a further 25 to 50% reduction in HC levels (Table 2).

Carbon monoxide emissions were generally correlated with PM emissions (Table 2), as previously reported.⁶ Both biodiesels gave comparable reductions of 40 to 45% in CO output relative to certification fuel.

Biodiesel is frequently used as a 20 volume percent blend with conventional diesel (so-called B-20). The soapstock methyl ester fuel was therefore also tested as a B-20 blend. The blend produced a small 1.5% NO_x increase (statistically significant at >99% confidence) and a 20% PM reduction relative to certification diesel (Table 2). Hydrocarbon and CO emissions with the B-20 blend were generally similar to those with petroleum diesel. These emissions levels are comparable to those of soybean oil methyl ester B-20 reported previously.⁵

Conclusions

By means of simple chemical methods, a low-quality under-utilized feedstock has been used to produce a biodiesel that is compositionally comparable and functionally identical to biodiesel produced from highly refined, food grade, soybean oil, but which may have a much lower cost.

Acknowledgment. We thank Cargill and the employees of its Gainesville, GA, refinery for soapstock, and Dr. Thomas A. Foglia for assistance in the determination of fatty acid ester contents by GC.

EF010051X