Fuel Properties and Nitrogen Oxide Emission Levels of Biodiesel Produced from Animal Fats

Victor T. Wyatt[a,*], Melissa A. Hess[a], Robert O. Dunn[b], Thomas A. Foglia[a], Michael J. Haas[a], and William N. Marmer[a]

[a]United States Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, Pennsylvania 19038, and [b]United States Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, Peoria, Illinois 61604

ABSTRACT: FAME of lard, beef tallow, and chicken fat were prepared by base-catalyzed transesterification for use as biodiesel fuels. Selected fuel properties of the neat fat-derived methyl esters (B100) were determined and found to meet ASTM specifications. The cold-flow properties, lubricity, and oxidative stability of the B100 fat-derived fuels also were measured. In general, the cold-flow properties of the fat-based fuels were less desirable than those of soy-based biodiesel, but the lubricity and oxidative stability of the fat-based biodiesels were comparable to or better than soy-based biodiesel. Nitrogen oxide (NO_x) emission tests also were conducted with the animal fat-derived esters and compared with soybean oil biodiesel as 20 vol% blends (B20) in petroleum diesel. The data indicated that the three animal fat-based B20 fuels had lower NO_x emission levels (3.2–6.2%) than did the soy-based B20 fuel.

Paper no. J11054 in *JAOCS 82*, 585–591 (August 2005).

KEY WORDS: Alkyl ester, biodiesel, chicken fat, cloud point, cold filter plugging point, high-frequency reciprocating rig, lard, NO_x emissions, oxidation stability, tallow.

The use of fats and oils as diesel engine fuels has been recognized since the advent of the diesel engine. Because of their high viscosities, however, it is now thought best to convert natural fats and oils into their simple alkyl ester derivatives to improve their viability as replacements for petroleum diesel fuel (1–4). This conversion is usually accomplished by alkali-catalyzed transesterification of the oil or fat with a simple alcohol, typically methanol, which converts their TAG into the corresponding simple FA alkyl ester derivatives. The success of transesterification depends on several factors, including the type of catalyst used, the mole ratio of alcohol to TAG used, the FFA content of the oil or fat, the water content, the reaction time (5), and mixing (6). The term "biodiesel" is now generally applied to these renewable alternative fuels when made from vegetable oils, animal fats, or recycled greases such as restaurant grease. In the United States, soybean oil methyl esters are the most common biodiesel fuel produced.

There is a growing interest in the use of biodiesel fuels since biodiesel offers several fuel advantages over petroleum diesel, including improved lubricity, a higher flash point, lower toxicity, biodegradability, and no net contribution to the greenhouse effect because it is made from renewable resources. Also, the increased use of these alternative fuels not only helps in our efforts to decrease dependency on foreign oil but also provides for a cleaner environment. Experimental data have shown that the addition of biodiesel to diesel fuel reduces particulate and carbon monoxide emissions but increases nitrogen oxide (NO_x) emissions (7,8). Pure soy biodiesel (B100) increases NO_x emissions by approximately 12% when compared with NO_x emission data for petroleum diesel. At the more widely used 20% blend level of biodiesel in petrodiesel, however, the increase in NO_x emissions is only on the order of 2–4%. With increasingly strict environmental regulations, even this relatively small increase in NO_x can negatively impact the use of biodiesel. Therefore, it may be of benefit to identify other feedstocks for producing a biodiesel that could improve NO_x emissions when blended with petroleum diesel.

Chicken fat, lard, and tallow are relatively inexpensive coproducts of their respective industries, yet only tallow is used in significant amounts in nonfood applications. These materials are readily available and can be suitable feedstocks for conversion to biodiesel. A major drawback of animal fat-based biodiesel, however, is that it generally has poorer cold-temperature properties than does vegetable oil-based biodiesel (9–12). Nevertheless, it is possible to improve the cold-flow properties of the esters through dry fractionation of the fat before esterification (13).

This study was intended to compare the fuel and NO_x emission levels of biodiesel produced from animal fats with existing data for soy biodiesel. Cold-temperature properties and other selected properties such as lubricity of the animal fat-derived biodiesel fuels also were compared with soy biodiesel and petroleum diesel.

MATERIALS AND METHODS

Materials. Edible beef tallow, refined lard, and rendered chicken fat were obtained from HRR Enterprises (La Porte, IN), Holsum Foods (Albert Lea, MN), and Tyson Foods (Springdale, AR), respectively. Certified diesel fuel was obtained from Chevron Phillips Chemical Company (Houston,

---

*To whom correspondence should be addressed at U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 East Mermaid Ln., Wyndmoor, PA 19038.
E-mail: vwyatt@errc.ars.usda.gov

TX). The fuel used was low sulfur (365 ppm) with a cetane number of 46.8. Soygold, a methyl soyate biodiesel, was purchased from Ag Environmental Products (Omaha, NE) in 1-gal units. Hexane, methanol, and isopropanol (HPLC grades) were purchased from Burdick and Jackson (Muskegon, WI). Anhydrous ether, 12 N hydrochloric acid, and glacial acetic acid were purchased from Mallinckrodt Chemicals (Phillipsburg, NJ).

Biodiesel synthesis. Typically, the animal fat (100–150 g) was melted and weighed into a bottle (500 mL with a Teflon-lined cap), and to this was added methanol (mole ratio of 6:1 methanol to fat) containing sodium hydroxide (0.4% w/w fat). The reaction mixture was shaken by hand to form an emulsion and then agitated in a Series 25 incubator shaker (New Brunswick Scientific Co. Inc., Edison, NJ) at 65°C for 30 min. After removal of the lower glycerol/methanol phase, an additional equivalent of methanolic sodium hydroxide solution was added to the mixture and the process was repeated. The FAME mixture was poured into a separatory funnel, diluted with an equal volume of ether, and washed with 5 N HCl (200 mL) and deionized water (2 × 200 mL). The organic layer was dried over anhydrous granular sodium carbonate, filtered, and the FAME isolated by removal of the solvent on a rotary evaporator to constant weight.

The percentages of FAME, FFA, and residual MAG, DAG, and TAG in the biodiesel fuels were determined by HPLC using methodology developed in our laboratory (14). Analyses were done with an HP Series 1050 high-performance liquid chromatograph (Agilent Technologies, Wilmington, DE) equipped with a cyanopropyl column (250 mm × 4.6 mm i.d., 5 µm; Phenomenex, Torrance, CA) and an ELSD (ELSD IIA; Varex, Burtonsville, MD). Lipid components were separated using a binary mobile phase of hexane and isopropanol, each containing acetic acid (0.4 vol/vol%). The fatty acyl composition of chicken fat, tallow, and lard methyl esters was determined by GC using an HP Model 5890 Series II GC with a split automatic injector, an FID, and an HP-INNOWAX column (30 m × 0.25 mm i.d., 5.3 µm film thickness; Agilent Technology. The column was held at 200°C for 2 min and then ramped to 260°C at 7°C/min. The carrier gas was helium at a rate of 1.0 mL/min.

Biodiesel acid value. Acid values for the animal fat-derived biofuels prepared in this study were determined following the method specified in ASTM Method D 664 (15).

Iodine value. Iodine values for the animal fat-derived biofuels prepared in this study were determined following the method specified in AOCS Official Method Cd 1-25 (16).

Kinematic viscosity. Viscosities were determined with a size 50 Cannon-Manning Semi-micro Viscometer from the Cannon Instrument Company (State College, PA) (17). The viscometer was calibrated with an S6 Cannon-certified viscosity standard and immersed in a constant-temperature kinematic viscosity bath (Series K23370; Koehler Instrument Company, Bohemia, NY). Silicone oil was used as the liquid medium. The viscosity bath was preheated to 40°C. The viscometer was charged with approximately 0.6 mL of methyl ester (biodiesel) and was allowed to equilibrate to the bath temperature (approx. 5 min). The sample was suctioned above the standard mark on the glass viscometer. A timer was used to record the efflux time required for the sample to flow freely from the calibration marks above and below the viscometer bubble. Experiments were performed in triplicate. The viscosity of the sample was calculated by multiplying the efflux time by the size 50 viscometer constant (0.004 mm^2/s).

Cloud point and pour point measurements. The cloud point (D 2500) and pour point (D 97) were determined manually for neat methyl esters and B20 fuels with a Koehler Instrument Company cloud and pour point bath in accordance with the corresponding ASTM specifications (18,19). Cloud point (D 5773) and pour point (D 5949) were determined automatically for neat methyl esters and B20 fuels in accordance with the corresponding ASTM specifications (20).

Crystallization onset temperature. A Perkin-Elmer (Norwalk, CT) Pyris 1 differential scanning calorimeter (DSC) attached to a nitrogen Dewar was used to obtain cooling and heating thermograms of the methyl esters. Cooling thermograms were obtained as follows: The esters were first heated to 60°C and held for 2 min, then cooled to −70°C at 10°C/min, held for 2 min at −70°C until the heat flow stabilized, and then heated from −70 to 60°C at 10°C/min.

High-frequency reciprocating rig (HFRR) testing. Diesel fuel lubricity was determined by HFRR testing in accordance with ASTM Method D 6079-99 (21).

Oxidative stability testing. The oxidative stability instrument used was manufactured by Omnion (Rockland, MA). Experiments were performed as prescribed in AOCS Method Cd 12b-92 (22).

NO_x emissions testing. A Yanmar L100 single-cylinder, four-stroke, naturally aspirated, air-cooled, direct-injection diesel engine from Bowers Power Systems (Kent, WA) was installed and instrumented for NO_x measurements. Details of the engine are as described by Hess *et al*. (23). The engine was connected by the manufacturer to an electrical generator. Load was added to the engine by using the generator to power ten 500-W work lights. The results discussed here were obtained at a load of 5 kW (82% maximum load) and an engine speed of 3200 rpm. These conditions were chosen to generate NO_x levels high enough to allow small changes in NO_x emission levels to be detected. NO and NO_2 were measured using model CA-CALC single gas monitors (TSI Instruments, Shoreview, MN) equipped with electrochemical sensors and calibrated weekly using calibration gases. The engine was considered to be at steady state when the exhaust temperature reached a constant temperature, as monitored with a thermocouple (Omega Instruments, Stanford, CT) inserted into the exhaust gas stream.

For each test, NO_x emission levels from petrodiesel were measured in triplicate against those from each B20 fuel on a run-to-run basis. Certified petrodiesel was used as received to bring the engine to steady state (as determined by a constant exhaust gas temperature) and to confirm the change in emissions on addition of the biodiesel blend. Engine speed was monitored with a tachometer and held at a constant speed and load for the duration of the test as NO$_x$ emissions of the petrodiesel were measured. The fuel was switched to B20 without disrupting the operation of the engine. The engine was run for a time sufficient to ensure that the petrodiesel was flushed from the system and that the engine was at a steady state. The NO$_x$ emissions from B20 were then measured and the percentage changes in NO$_x$ from experiment to experiment were compared.

RESULTS AND DISCUSSION

Methyl esters were produced from each of the animal fat feedstocks in high yield. Because methanol and animal fats are immiscible, it was imperative to achieve adequate mixing to produce high ester yields. Stirring the solution with a magnetic stir bar did not sufficiently generate an emulsion, resulting in a low conversion of TAG to methyl esters. Therefore, the solutions had to be vigorously shaken mechanically to generate an emulsion to facilitate transesterification. In this way, and by following the two-step procedure reported by Freedman *et al*. (24), high conversions (>98%) of the animal fats into their respective methyl ester derivatives were achieved. Each reaction mixture resulted in a two-phase system that mainly consisted of glycerol (bottom layer) and a methyl ester phase (top layer). After isolation, the methyl ester layer was washed with dilute HCl to neutralize the alkali catalyst and then water to remove residual traces of methanol and glycerol. After drying, the FAME distribution of the biofuels was determined, and selected biofuel properties and NO$_x$ emission tests were conducted.

Table 1 lists the FAME composition for the biodiesel fuels produced from the animal fats and, for comparison purposes, the FAME composition of soy biodiesel. FAME profiles for the animal fat esters were similar to each other, with oleic acid being the predominant FA (41–44%) in the three fats. For FAME from tallow and lard, palmitic acid (~23%) was the next most abundant FA, followed by stearic acid (~13%). For FAME from chicken fat, palmitic and linoleic acids were of the same magnitude (~20%), as were palmitoleic and stearic acids (~5%). The fatty acyl composition of the three animal fat-based methyl esters differed from soy-based biodiesel in that for soy biodiesel, linoleic acid (~52%) was the predominant FA, followed by oleic (~21%) and palmitic (~11%) acids. Chicken fat FAME had the higher amount of total unsaturated FA (UFA, ~67%) of the animal fat esters, whereas lard and tallow FAME had comparable amounts of UFA (52–55%). For total saturated FA (SFA), the opposite was observed, with SFA being ~38% for lard and tallow and ~27% for chicken fat. Soy biodiesel had a higher amount of UFA (~81%) than did any of the animal fat esters. This may be significant when considering the benefits of a biodiesel produced from animal fats compared with a soy-based biodiesel. Unsaturated fats are more susceptible to chemical deterioration (e.g., autoxidation and polymerization) under certain conditions. This is an important concern when thermal stability is considered. Table 1 also shows that, as expected, the iodine value increased with the degree of unsaturation (25). Some research has reported that the degree of unsaturation does not lead to decreased oxidative stability during storage (26–28), but other work has found that high unsaturation levels in a fuel can lead to the formation of engine deposits and to deterioration of the engine lubricating oil (29). Research is presently underway to ascertain whether a significant correlation exists between unsaturation and fuel stability, and engine performance.

Experimental data for selected fuel properties of the fat-derived biodiesels are listed in Table 2. The fuels were prepared in our laboratory and tested by a commercial fuel testing facility (Magellan Analytical Services, Kansas City, KS) to verify that they met ASTM specifications (30). Neat biodiesels produced from the animal fats were analyzed for viscosity, acid number, flash point, free and total glycerin, copper corrosion, sulfated ash, and residual water and sediment and were found to be within ASTM specifications. Viscosities for the animal fat-derived FAME, in general, were slightly higher than that for the soy-based esters but were within the specified limit.

TABLE 1
Fatty Acyl Distribution and Iodine Value for FAME Derived from Animal Fats and Oils

	FAME composition (wt)%			
FA	Tallow	Lard	Chicken fat	Soybean oil
C14:0	3.1	1.3	0.7	0
C14:1	1.3	0.0	0.13	0
C15:0	0.5	0.0	0.0	0.0
C16:0	23.8	23.5	20.9	10.6
C16:1	4.7	2.6	5.4	0
C17:0	1.1	0.4	0.0	0.0
C18:0	12.7	13.5	5.6	4.6
C18.1	47.2	41.7	40.9	22.1
C18.2	2.6	10.7	20.5	54.2
C18.3	0.8	0.0	0.0	7.5
Sum (%)	98.8	98.7	99.4	99.0
ΣSFA (%)[a]	38.2	38.3	27.2	16.2
ΣUFA (%)[a]	52.6	55.0	67.0	82.8
Iodine value	53.6 ± 0.2	62.5 ± 0.1	77.4 ± 0.4	129.1 ± 1.0

[a] UFA is the sum of unsaturated FA; SFA is the sum of saturated FA.

TABLE 2
Selected Physical Properties for Methyl Esters (ME) Produced from Animal Fats

Physical property[a]	ASTM method	ASTM specification[b]	ME		
			LME	TME	CFME
Viscosity (mm^2/s)	D 445	1.9–6.0	4.8	5.0	4.3
Acid number (mg KOH/g)	D 664	0.80	0.49	0.44	0.33
Flash point (°C)	D 93	130 min	160	150	150
Free glycerin (mass %)	D 6584	0.020	0.008	0.016	0.004
Total glycerin (mass %)	D 6584	0.240	0.182	0.167	0.101
Water and sediment (% volume)	D 2709	0.050	0.005	0.030	0.020
Copper corrosion	D 130	No. 3 max	1[a]	1[a]	1[a]
Sulfated ash (mass %)	D 874	0.020 max	0.003	0.009	0.006

[a] All measurements except for acid number were conducted by Magellan Analytical Services (Kansas City, KS). LME, lard methyl esters; TME, tallow methyl esters; CFME, chicken fat methyl esters.
[b] Specification as given in Reference 30.

This may reflect the higher saturated fatty ester content of the former esters, but there was no correlation between the saturated fatty ester content of the esters and viscosity. Acid numbers were prescreened on-site before the samples were shipped for testing. It was necessary to lower the acid number for each sample because initial results indicated that our procedure produced biodiesel that did not meet the ASTM specification for acid number. It is unknown whether the high acid value is a reflection of high amounts of FFA or whether it is a measure of residual acid from the acid washes. The acid wash is important to perform after transesterification to remove the alkali catalyst and eliminate emulsion problems caused by soap formation. It was likely that the high acid numbers resulted from the formation of FFA, which are miscible in the esters and hence increased their acid numbers. It should be noted that, in general, the flash points of the animal fat-derived methyl esters were lower than values typically reported for vegetable-based methyl esters, but they met the ASTM specification and were still considerably higher than those of petroleum-based biodiesel.

The cloud points, pour points, and cold-filter plugging points (CFPP) of the animal fat esters are listed in Table 3 along with similar values reported for soy biodiesel (11,12) and petrodiesel (10). Although there is no prescribed biodiesel specification for cloud point, it is used as a measure of the low-temperature performance of a biodiesel fuel. In general, biodiesel fuels produced from the animal fats listed in Table 3 had cloud and pour points higher than the values determined for the soybean oil-based biodiesel. Consistently higher cloud point and pour point temperatures were observed for biodiesel when using the automatic method (20). This is likely a result of the increased sensitivity of the automatic method in detecting very small crystals at higher temperatures. All reported values, however, were within the normal reproducibility limits of the same material for cloud point and pour point. More interesting is the observation that the cloud point was lower than the pour point for the chicken fat and lard methyl esters. This resulted from the methodology used in determining the pour point. Samples were typically monitored in 2–3°C intervals until a temperature was reached at which no motion of the fuel was detected. The pour point was then defined as 2–3°C higher than that temperature. Petroleum fluids typically have a 10–15°C variance between the cloud point and pour point. In contrast, the cloud point and pour point of a given biodiesel are generally very close to each other, meaning that pour points can be, by definition, as high as 3°C above the corresponding cloud point. Previous work has shown that blending biodiesel fuels (B20) with petrodiesel ameliorates their cold-temperature properties to levels that are comparable to neat petrodiesel (10,11). Cloud point and pour point temperatures for 20% blends (B20) of the animal fat-derived biodiesels (shown in Table 3) were as much as 24°C lower than their neat (B100) counterparts. It is also possible to improve the cold-temperature properties of neat biodiesel through dry fractionation, which removes saturated fatty esters before or after transesterification (13).

Onset crystallization temperatures (T_{co}) for the animal fat-derived esters were determined since they can be used as an additional indicator to predict cloud point (11). Cloud points were typically lower than the T_{co} measured by DSC, which suggests that DSC is a more sensitive method for detecting the presence of crystals in the esters. As anticipated, the heating thermograms for the lard and chicken fat methyl esters (see Table 3) were higher than their corresponding cloud points, but within error, the T_{co} and cloud point for tallow methyl esters were the same. Previous reports indicated that melting thermograms gave a higher T_{co} than did the corresponding cooling thermograms, making the former a better predictor of the cold-temperature properties of a biodiesel (31).

A more important measure of diesel fuel cold-flow operability, however, is the CFPP, which more accurately reflects the cold-flow operability of the fuel. As listed in Table 3, the CFPP for both lard and tallow were approximately 10°C higher than for soy biodiesel, whereas for the chicken fat biodiesel, the difference was only 4°C higher. These results were not unexpected since, compared with soy-based biodiesel, the animal fat-based esters have a higher content of SFA. The latter have higher m.p. than do UFA of similar chain lengths and hence are more readily precipitated at lower temperatures.

TABLE 3
Low-Temperature Properties of ME Produced from Animal Fats and Soybean Oil

	Fuel^a				
Property	LME	TME	CFME	SME^{b,d}	No. 2 diesel (D)^{c,d}
Cloud point (°C)	11.0 ± 0.0^d	11.0 ± 0.0^d	4.3 ± 0.3^d	1.0 to 2.0	−16
	12.4 ± 0.1^e	12.8 ± 0.2^e	5.6 ± 0.1^e		
Pour point (°C)	12 ± 0.0^d	9.0 ± 0.0^d	6.0 ± 0.0^d	−2.0 to −4.0	−27
	13.7 ± 0.3^e	13.0 ± 0.0^e	8.0 ± 1.0^e		
Cloud point^d (°C)					
ME/D (20:80 vol/vol blend)	−8.8 ± 0.8	−9.9 ± 1.2	−10.3 ± 0.8	−11 ± 1.8	—
Pour point^d (°C)					
ME/D (20:80 vol/vol blend)	−10.1 ± 2.0	−11.1 ± 0.7	−13.7 ± 1.6	−18 ± 1.6	—
CFPP^f (°C)	8.3 ± 0.3	8.0 ± 1.0	1.3 ± 0.3	−3.3 ± 0.3	−27
Viscosity^g (Cs/s)	4.8	5.0	5.4	4.3	2.8
T_{co} (°C)	16.0 ± 0.05	12.9 ± 0.05	10.3 ± 0.2	5.2^h	−11.9^h

[a] Fuels are 100% biodiesel (B100) unless otherwise stated. SME, soybean oil methyl esters; CFPP, cold-filter plugging point; T_{co}, onset time of crystallization; for other abbreviations see Table 2.
[b] Data for cloud point, pour point, and viscosity were taken from Reference 9.
[c] Data were taken from Reference 10.
[d] Indicates manual determination of the cloud point and pour point according to ASTM Methods D 2500 (18) and D 97 (19).
[e] Indicates automatic determination of the cloud point and pour point according to ASTM Methods D 5773 and D 5949 (20).
[f] CFPP determinations were performed by Dunn and Bagby (11) at the National Center for Agricultural Utilization Research (Peoria, IL).
[g] ASTM D 445 specification for the viscosity of B100 is 1.8–6.9 Cs/s (17).
[h] Data were taken from References 11 and 12.

Previous work has shown that soy-derived methyl esters have better lubricity than does petroleum diesel, and their use as additives for enhancing the lubricity of petroleum diesel has been suggested (32). Lubricity data for the neat fat-derived methyl esters as measured by HFRR are listed in Table 4. A lower wear scar indicates better lubricity, and based on this test, it is recommended that all diesel fuels have a wear scar diameter no higher than 460 microns (33). The data indicate that the animal fat-derived methyl esters also have better lubricity than does petroleum diesel, with lubricity increasing as the degree of unsaturation increases. Other researchers have reported enhanced lubricity with increasing concentrations of hydroxylated esters (34). Other factors, including the free glycerin content of the biodiesel, can affect its lubricity. The animal fat-derived methyl esters were all within the ASTM specification for both free and total glycerin (Table 2).

Oxidative stabilities of the animal fat-derived esters were determined experimentally and are summarized in Table 4. Oxidative stability is a measure of the degree of resistance to oxidation and depends on the degree of unsaturation, the position of the double bonds along the FA chain (35,36), natural or added antioxidants, pro-oxidants, or prior abuse. No antioxidants were added to our samples. Iodine values (measures of the degree of unsaturation), for the fat-derived esters are listed in Table 1 and can be used to estimate their relative oxidative stability. In general, oxidative stability increased with an increase in the SFA content of the biodiesel, but the chicken fat FAME was anomalous.

The NO_x emissions found for the 20% biodiesel blends produced from animal fats and for soy biodiesel, when compared with petrodiesel, are shown in Table 5. The data listed are expressed as the average (four determinations at a confidence level of $P \geq 0.05$) percentage increase over petrodiesel and as the average percentage decrease of the animal fat biodiesels when compared with soy biodiesel. The B20 soy biodiesel increased NO_x emissions by 6.2% over that observed with petrodiesel. In general, all the animal fat biodiesels had lower NO_x levels than did the soy biodiesel. The chicken fat and refined lard showed decreased NO_x emissions when compared with soy biodiesel but still showed an increase in NO_x emissions over those for petrodiesel. For the B20 tallow blend, how-

TABLE 4
Lubricity and Oxidative Stability of ME Produced from Fats and Oils^a

Ester	Average wear scar (μm)^b	OSI^c
TME	219 ± 9	69 ± 13
CFME	311 ± 13	3.5 ± 0.9
LME	206 ± 4	18.4 ± 4.6
SME	195 ± 4	7.9 ± 0.4
No. 2 D	376	ND^d

[a] Data listed are the results obtained for all ME prepared in house from commercially obtained animal fats and oils.
[b] High-frequency reciprocating rig lubricity was determined by ASTM Method D 6079 (21).
[c] Oil stability index (OSI) was determined by AOCS Method Cd 12b-92 (22).
[d] ND, not determined; for other abbreviations see Tables 2 and 3.

TABLE 5
NO_x Emissions of Animal Fat- and Soy-Derived ME Blended in Petroleum Biodiesel at the 20% Level (B20)

B20 biodiesel blend^a	Increase in NO_X emissions^b (%)	Decrease in NO_X emissions relative to B20 soy blend (%)
SME	6.2 (± 1.7)	—
LME	3.0 (± 0.3)	−3.2 (± 0.8)
CFME	2.4 (± 0.8)	−3.8 (± 0.8)
TME	0.0 (± 1.1)	−6.2 (± 1.1)

[a] B20 is a 20 vol/vol% blend of the oil or fat biodiesel listed and diesel fuel.
[b] Data listed are the average percentage increases in NO_x over petrodiesel; $n = 4$, $P > 0.05$. NO_x, nitrogen oxide; for other abbreviations see Tables 2 and 3.

ever, NO_x emissions were within the experimental error for petrodiesel. This indicated that under the conditions used here, the tallow biodiesel was NO_x neutral. This NO_x decrease is significant because it eliminates the increase in NO_x emissions observed when a 20% blend of soy biodiesel is substituted for petrodiesel. This suggests that by judiciously blending biofuels from various feedstocks, a NO_x-neutral biodiesel fuel can be formulated. These engine tests were intended to use NO_x emissions as an indicator in simple, inexpensive screens to determine the viability of animal fat-derived biodiesel as an alternative to vegetable oil-derived biodiesel. These experiments were performed at a single speed and load and were therefore not designed to give emissions data over all engine conditions. A more complete analysis would require transient engine tests to measure carbon monoxide and particulate emissions to see whether they would improve with an improvement in NO_x emissions.

Under the test conditions reported herein, we have demonstrated that B20 blends of methyl esters of animal fats in petrodiesel have lower NO_x emissions than B20 blends of methyl esters produced from soy oil. Additionally, for the test engine used in this study, the beef tallow methyl esters did not increase NO_x emission levels above those measured for petrodiesel. The methyl esters produced from chicken fat, lard, and beef tallow had poorer low-temperature properties than did the soy methyl esters, but this difference among the esters was minimized when blended at the 20% level in petrodiesel. Since the animal fat-derived esters can be NO_x neutral, they should be considered as alternatives to soy biodiesel in fuel blends or as fuel additives.

ACKNOWLEDGMENTS

The technical assistance of Pamela S. Fox, Becky Sanders, Kerby C. Jones, and Jacqueline Shea is acknowledged. Mention of trade names or commercial products in this article is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

REFERENCES

1. Bruwer, J.J., B.v.D. Boshoff, F.J.C. Hugo, J. Fuls, C. Hawkins, A.N.v.d. Walt, and L.M. du Plessis, *Agricultural Energy*, ASAE Publication 4-81, American Society of Agricultural Engineers, St Joseph, MI, 1981, Vol. 2, pp. 385–390.
2. Clark S.J., L. Wagner, M.D. Schrock, and P.G. Piennaar, Methyl and Ethyl Soybean Esters as Renewable Fuels for Diesel, *J. Am. Oil Chem. Soc. 61*:1632–1637 (1984).
3. Natusch, D.F.S., D.W. Richardson, and R.J. Joyce, Methyl Esters of Tallow as a Diesel Extender, in *Proceedings of the VI International Symposium on Alcohol Fuels Technology Conference* (May 21–25, 1984), Ottawa, Canada, 1984, Vol. 1, pp. 340–346.
4. Ali, Y., M.A. Hanna, and S.L. Cuppett, Fuel Properties of Tallow and Soybean Oil Esters, *J. Am. Oil Chem. Soc. 72*:1557–1564 (1995).
5. Ma, F., L.D. Clements, and M.A. Hanna, The Effects of Catalysts, Free Fatty Acids, and Water on Transesterification of Beef Tallow, *Trans. ASAE 41*:1261–1264 (1998).
6. Ma, F., L.D. Clements, and M.A. Hanna, The Effect of Mixing on Transesterification of Beef Tallow, *Bioresour. Technol. 69*:289–293 (1999).
7. Graboski, M.S., and R.L. McCormick, Combustion of Fat and Vegetable Oil Derived Fuels in Diesel Engines, *Prog. Energy. Comb. Sci. 24*:125–164 (1998).
8. American Biofuels Association Information Resources, *Biodiesel: A Technology Performance and Regulatory Overview*, National Soy Diesel Development Board, Jefferson City, MO, 1994.
9. Foglia, T.A., L.A. Nelson, R.O. Dunn, and W.N. Marmer, Low-Temperature Properties of Alkyl Esters of Tallow and Grease, *J. Am. Oil Chem. Soc. 77*:951–955 (1997).
10. Wu, W.-H., T.A. Foglia, W.N. Marmer, R.O. Dunn, C.E. Goering, and T.E. Briggs, Low-Temperature Property and Engine Performance Evaluation of Ethyl and Isopropyl Esters of Tallow and Grease, *Ibid. 75*:1173–1177 (1998).
11. Dunn, R.O., and M.O. Bagby, Low-Temperature Properties of Triglyceride-Based Diesel Fuels: Transesterified Methyl Ester and Petroleum Middle Distillate/Ester Blends, *Ibid. 72*:895–904 (1995).
12. Bagby, M.O., Inks, Biofuels, and Other Emerging Products from Vegetable Oils, in *Proceedings of the 9th International Conference on Jojoba and Its Uses*: *Third International Conference on New Industrial Crop Products*, edited by L.H. Princen, and C. Rossi, Association for the Advancement of Industrial Crops, Phoenix, AZ, 1996, pp. 220–224.
13. Lee, K.-T., T.A. Foglia, and K.-S. Chang, Production of Alkyl Ester as Biodiesel from Fractionated Lard and Restaurant Grease, *J. Am. Oil Chem. Soc. 79*:191–195 (2002).
14. Foglia, T.A., K.C. Jones, A. Nuñez, J.G. Phillips, and M. Mittelbach, Comparison of Chromatographic Methods for the Determination of Bound Glycerol in Biodiesel, *Chromatographia 60*:305–311 (2004).
15. ASTM, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, D 664-01, ASTM International, West Conshohocken, PA, 2003.
16. AOCS, Iodine Value of Fats and Oils (Wijs method), in *Official Methods and Recommended Practices of the AOCS*, 5th edn., edited by D. Firestone, AOCS Press, Champaign, 1999, Method Cd 1-25.
17. ASTM, Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the calculation of dynamic viscosity), D 445, ASTM International, West Conshohocken, PA, 2003.
18. ASTM, Test Method for Cloud Point of Petroleum Products, D 2500, ASTM International, West Conshohocken, PA, 2002.
19. ASTM, Test Method for Pour Point of Petroleum Products, D 97-96a, ASTM International, West Conshohocken, PA, 1998.
20. ASTM, *Annual ASTM Book of Standards, Volume 05.03: Petroleum Products and Lubricants*, ASTM International, West Conshohocken, PA, 2003, Methods D 5773, D 5949.
21. ASTM, Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR), D 6079-99, ASTM International, West Conshohocken, PA, 1999.
22. AOCS, Fat Stability, Active Oxygen Method, in *Official Methods and Recommended Practices of the AOCS*, 5th edn., edited by D. Firestone, AOCS Press, Champaign, 1999, Method Cd 12b-92.
23. Hess, M.A., M.J. Haas, T.A. Foglia, and W.N. Marmer, The Effect of Antioxidant Addition on NO_x Emissions from Biodiesel, *Energy Fuels 19*:1749–1754.
24. Freedman, B., E.H. Pryde, and T.L. Mounts, Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils, *J. Am. Oil Chem. Soc. 61*:1638–1643 (1984).
25. Bockisch, M., *Fats and Oils Handbook*, AOCS Press, Champaign, IL, 1998.
26. Howell, S., U.S. Biodiesel Standards—An Update of Current Activities, SAE Technical Paper Series 971687, in *State of Alternative Fuel Technologies*, publication SP-1274, Society of Automotive Engineers, Warrendale, PA, 1997, pp. 203–208.

27. Graboski, M.S., R.L. McCormick, T.L. Alleman, and A.M. Herring, Effect of Biodiesel Composition on the NO_x and PM Emissions from a DDC Series 60 Engine*,* final report to the National Renewable Energy Laboratory, Colorado Institute for Fuels and Engine Research, Golden, CO, December 29, 1999.
28. McCormick, R.L., M.S. Graboski, T.L. Alleman, A.M. Herring, and K.S. Tyson, Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine, *Environ. Sci. Technol*. *35*:1749–1747 (2001).
29. Mittelbach, M., Diesel Fuel Derived from Vegetable Oils, VI: Specifications and Quality Control of Biodiesel, *Bioresour. Technol. 56*:7–11 (1996).
30. ASTM, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, Designation D 6751–02, ASTM International, West Conshohocken, PA, 2002.
31. Lee, I., L.A. Johnson, and E.G. Hammond, Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel, *J. Am. Oil Chem. Soc. 72*:1155–1160 (1995).
32. Van Gerpen, J., S. Soylu, and D. Chang, Evaluation of Lubricity of Soybean Oil-based Additives in Diesel Fuel, manuscript prepared for The United Soybean Board, Iowa State University, Ames, IA, 1998.
33. Dresel Fuel Technical Review, Chevron U.S.A., Inc., San Francisco, 1998.
34. Goodrum, J.W., and D.P. Geller, Effects of Specific Fatty Acid Methyl Esters on Diesel Fuel Lubricity, *Fuel 82*:2351–2356 (2004).
35. Knothe, G., and R.O. Dunn, Dependence of Oil Stability Index of Fatty Compounds on Their Structure and Concentration and Presence of Metals, *J. Am. Oil Chem. Soc. 80*:1021–1026 (2003).
36. Knothe, G., and R.O. Dunn, Structure Indices in Fatty Acid Chemistry. How Relevant Is the Iodine Value? *Ibid. 79*:847–854 (2002).

[Received February 8, 2005; accepted July 7, 2005]