

# Preparation of Fatty Acid Methyl Esters from Osage Orange (*Maclura pomifera*) Oil and Evaluation as Biodiesel

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**ABSTRACT:** Fatty acid methyl esters were prepared in high yield by transesterification of osage orange (*Maclura pomifera* L.) seed oil. The crude oil was extracted using supercritical CO<sub>2</sub> and was initially treated with mineral acid and methanol to lower its content of free fatty acids, thus rendering it amenable to homogeneous, alkali-catalyzed methanolysis. The principle components identified in osage orange methyl esters (OOMEs) were methyl linoleate (76.4%), methyl oleate (11.9%), methyl palmitate (7.0%), and methyl stearate (2.4%). As a result of the high content of methyl linoleate, OOMEs exhibited cetane number (44.9) and induction period (IP; 2.4 h) values below the ranges specified in the biodiesel standards ASTM D6751 and EN 14214. The addition of 500 ppm *tert*-butylhydroquinone (TBHQ) resulted in a higher IP (6.4 h) compliant with the biodiesel standards. Furthermore, the high content of methyl linoleate resulted in an iodine value (IV; 144 g of I<sub>2</sub>/100 g) in excess of the maximum limit specified in EN 14214. The acid value (AV), glycerol content, kinematic viscosity, moisture content, phosphorus content, and sulfur content of OOMEs were within the limits prescribed in ASTM D6751 and EN 14214. In addition, data collected for density, lubricity, and energy content were typical for biodiesel fuels. The cold-flow properties of OOMEs were superior to those reported for several other biodiesel fuels. Also investigated were B5 and B20 blends of OOMEs in petrodiesel, which yielded AVs, kinematic viscosities, moisture contents, sulfur contents, lubricities, and densities within the limits prescribed in the petrodiesel standards. The addition of 500 ppm TBHQ to the blends resulted in IPs above the minimum thresholds specified in ASTM D7467 and EN 590. In summary, osage orange seeds provide a low-cost, non-food, high-oil-producing feedstock suitable for production of biodiesel.

## 1. INTRODUCTION

Biodiesel is defined as monoalkyl esters of long-chain fatty acids (FAs) prepared from lipids.<sup>1,2</sup> Advantages of biodiesel over petroleum diesel fuel (petrodiesel) include derivation from renewable feedstocks, displacement of imported petroleum, superior biodegradability, inherently good lubricity, lower toxicity, positive energy balance, lower exhaust emissions, negligible sulfur content, and higher flash point. Disadvantages include poor economics, limited feedstock availability, inferior cold-flow properties, lower volumetric energy content, and inferior oxidative stability.<sup>2</sup> Biodiesel must comply with fuel standards (Table 1), such as American Society for Testing and Materials (ASTM) D6751 or the Committee for Standardization (CEN) standard EN 14214, before its commercial use is approved in diesel engines.<sup>1,3</sup> Although biodiesel can be used directly in modern unmodified diesel engines, it is more commonly encountered in on-highway applications as a blend component in petrodiesel. Currently, blends up to B5 (5 vol % in petrodiesel) are permitted in ASTM D975, the U.S. petrodiesel standard.<sup>4</sup> In addition, B6–B20 blends are covered by ASTM D7467 (Table 2).<sup>5</sup> Biodiesel must meet the requirements of ASTM D6751 before its use as a blend component in petrodiesel. Moreover, the European petrodiesel standard EN 590 permits blending of biodiesel conforming to EN 14214 up to the B7 level (Table 2).<sup>6</sup>

Lipid availability varies according to geography, climate, and economics. Thus, canola oil is principally used in Europe; palm

oil predominates in tropical countries; and soybean oil and animal fats are primarily used in the U.S.<sup>2</sup> However, the combined supply of these lipids is sufficient to displace only a small percentage of petrodiesel. For example, if all U.S. soybean production were dedicated to biodiesel, an estimated 6% of petrodiesel demand would be displaced.<sup>7</sup> Consequently, alternative feedstocks have attracted considerable attention, as evidenced by recent reports of biodiesel prepared from field pennycress (*Thlaspi arvense* L.), moringa (*Moringa oleifera* L.), and camelina (*Camelina sativa* L.) seed oils, among numerous others.<sup>2,8–10</sup> Desirable characteristics of oilseed feedstocks include adaptability to local growing conditions, regional availability, high oil content, favorable FA composition, compatibility with existing farm practices, low agricultural inputs, definable growing season, uniform seed maturation rates, potential markets for byproducts, compatibility with fallow lands, and rotational adaptability with commodity crops.<sup>2,8,10</sup> Biodiesel prepared from feedstocks that meet all or most of these criteria hold the greatest promise as alternatives to petrodiesel.

*Maclura pomifera*, colloquially referred to as osage orange, is probably native to southeastern regions in the U.S. that overlap with the historical lands of the Osage Nation. The tree was widely planted as a wind break or hedge along fence lines and is easily

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**Table 1. Properties of Osage Orange Seed Oil Methyl Esters (OOMEs) with a Comparison to Standards**

	ASTM D6751	EN 14214	OOMEs
acid value (mg of KOH/g)	0.50 maximum	0.50 maximum	0.11 (0.02) <sup>d</sup>
glycerol content			
free (mass %)	0.020 maximum	0.020 maximum	0.007
total (mass %)	0.240 maximum	0.250 maximum	0.142
cold-flow properties			
CP (°C)	report	<i>b</i>	3.8 (0.8)
CFPP (°C)	<i>b</i>	variable <sup>c</sup>	−8.7 (0.6)
PP (°C)	<i>b</i>	<i>b</i>	−12.0 (0)
oxidative stability			
IP at 110 °C (h)	3 minimum	6 minimum	2.4 (0.1)/4.1 (0.1) <sup>d</sup> /6.4 (0.2) <sup>e</sup>
OT (°C)	<i>b</i>	<i>b</i>	164.9 (0.4)
PV (mequiv/kg)	<i>b</i>	<i>b</i>	9.82 (0.28)
iodine value (g of I <sub>2</sub> /100 g)	<i>b</i>	120 maximum	144
kinematic viscosity			
at 40 °C (mm <sup>2</sup> /s)	1.9–6.0	3.5–5.0	4.40 (0.02)
cetane number	47 minimum	51 minimum	44.9 (0.9) <sup>f</sup>
sulfur (ppm)	15 maximum	10 maximum	6.0
phosphorus (mass %)	0.001 maximum	0.001 maximum	<i>g</i>
moisture content (ppm)	<i>b</i>	500 maximum	478 (3)
wear scar at 60 °C (μm)	<i>b</i>	<i>b</i>	155 (8)
density			
at 15.6 °C (kg/m <sup>3</sup> )	<i>b</i>	860–900	892 (1)
at 40 °C (kg/m <sup>3</sup> )	<i>b</i>	<i>b</i>	890 (1)
HHV (MJ/kg)	<i>b</i>	<i>b</i>	39.47 (0.13)
Gardner color	<i>b</i>	<i>b</i>	5

<sup>a</sup> Values in parentheses are standard deviations from the reported means. <sup>b</sup> Not specified. <sup>c</sup> Variable by location and time of year. <sup>d</sup> With 250 ppm TBHQ added. <sup>e</sup> With 500 ppm TBHQ added. <sup>f</sup> Derived cetane number. <sup>g</sup> Not detected.

recognized by its distinctive large green fruit (hedge or horse apple). Belonging to the Moraceae family, it grows relatively fast, is drought-tolerant, and can flourish in a wide range of soil types as well as soil moisture conditions. The United States Department of Agriculture (USDA) hardiness classification for osage orange is 5–9, which encompasses nearly all of the lower 48 states, with the exception of the northern plains, the northern Rocky Mountains, parts of California and Florida, and the mountainous regions of New England. Irrigation is not required, as long as the tree receives 24–40 in. of rainfall per year.<sup>11</sup> The deciduous tree bears fruit at 10 years of age, lives 150 years or more, and can reach a height of 9–12 m. The wood is noted for its great durability, hardness, density, and resistance to decay, insects, and disease. Other than its uses as a hedge and for hardwood, the inedible fruit (10–13 cm) has been used for years as an insect repellent around homes.<sup>12–16</sup>

Seeds comprise approximately 11% of the mass of osage orange fruit and are composed of 5.9% moisture, 6.7% ash, 20.8% carbohydrates, 33.9% protein, and 32.8% fat.<sup>12</sup> The FA profile, tocopherol and phytosterol contents, and selected chemical and physical properties of the lipid from osage orange have been reported.<sup>12</sup> The yield of fruit/year is reported to be up to 450 kg/tree, which equates to 49.5 kg of seeds (16.2 kg of plant oil) per tree per year.<sup>13</sup> The tree can be planted at high density, such as 100 trees/ha.<sup>14</sup> Assuming 100 trees/ha that each produce 16.2 kg of lipid/year, the maximum yield of plant oil/year is calculated to be 1800 L/ha. For comparison, classic oilseeds, such as camelina, rapeseed, soybean, and sunflower, yield around 900,

1340, 560, and 750 L per hectare per year.<sup>17</sup> Osage orange was of interest as a feedstock for biodiesel production because of its potential to produce a large amount of lipid per hectare per year.

Traditional extraction of plant oils involves organic solvents, such as hexane. Hexane is advantageous because it readily solubilizes lipids, is abundantly available, and has a relatively high vapor pressure, ensuring its ease of evaporation. However, disadvantages include flammability, toxicity, price volatility linked to petroleum prices, increasing regulatory pressures on emissions, and retardation of extraction efficiency as a result of mass-transfer limitations between liquid and solid phases. Supercritical (SC) fluids, such as CO<sub>2</sub> (SC-CO<sub>2</sub>), are suitable as hexane substitutes for extraction, thus making them attractive as environmentally friendly alternatives to toxic and flammable organic solvents. The disadvantages of hexane are ameliorated with SC-CO<sub>2</sub>, owing to the unique properties of SC fluids. Limitations to the SC approach include higher temperature and pressure requirements, which equate to increased energy costs and the need for specialized equipment to handle such conditions.<sup>18,19</sup> Because of the increased economic and energy costs associated with the use of SC fluids, commercial extraction of lipids to be used for production of relatively low-value products, such as biodiesel, is normally accomplished using hexane or expeller (screw press) extraction methodologies. Commercial extraction using SC fluids in the U.S. is typically reserved for high-value food-related materials, such as hops and caffeine from decaffeinated coffee, where exposure to toxic organic solvents is undesirable. The SC approach was of

Table 2. Properties of OOMEs Blended with ULSD Fuel with a Comparison to Petrodiesel Standards

	petrodiesel standards			blends of OOMEs in ULSD		
	ASTM D975	ASTM D7467	EN 590	B0	B5	B20
biodiesel content (vol %)	0–5	6–20	0–7	0	5	20
acid value (mg of KOH/g)	<i>a</i>	0.30 maximum	<i>a</i>	0.01 (0.01) <sup>b</sup>	0.01 (0.01)	0.01 (0.01)
moisture content (ppm)	<i>a</i>	<i>a</i>	200 maximum	17 (1)	22 (1)	55 (2)
cold-flow properties						
CP (°C)	<i>c</i>	<i>c</i>	<i>a</i>	−17.5 (0.1)	−13.7 (0.3)	−12.7 (0.2)
CFPP (°C)	<i>c</i>	<i>c</i>	<i>a</i>	−18.0 (0)	−18.0 (0)	−17.7 (0)
PP (°C)	<i>a</i>	<i>a</i>	<i>a</i>	−24.0 (0)	−24.0 (0)	−20.0 (0)
oxidative stability						
IP at 110 °C (h)	<i>a</i>	6 minimum	20 minimum	40.1 (1.5)	11.9 (0.2)/43.5 (1.0) <sup>d</sup>	5.7 (0.1)/17.3 (0.4) <sup>d</sup>
kinematic viscosity						
at 40 °C (mm <sup>2</sup> /s)	1.9–4.1	1.9–4.1	2.0–4.0	2.30 (0.01)	2.34 (0.01)	2.57 (0.01)
sulfur (ppm)	15 maximum	15 maximum	10 maximum	9	8	7
wear scar at 60 °C (μm)	520 maximum	520 maximum	460 maximum	571 (4)	233 (4)	160 (5)
density						
at 15.6 °C (kg/m <sup>3</sup> )	<i>a</i>	<i>a</i>	820–845	837 (1)	839 (0)	855 (0)
at 40 °C (kg/m <sup>3</sup> )	<i>a</i>	<i>a</i>	<i>a</i>	821 (0)	822 (0)	838 (0)
HHV (MJ/kg)	<i>a</i>	<i>a</i>	<i>a</i>	46.23 (0.10)	45.18 (0.14)	44.24 (0.11)

<sup>a</sup> Not specified. <sup>b</sup> Values in parentheses are standard deviations. For sulfur content, *n* = 1. <sup>c</sup> No limits are specified, but guidance is provided. <sup>d</sup> With 500 ppm TBHQ added.

interest in the current study because of its safety advantages over hexane-mediated extraction. Recent examples of lipids extracted on the laboratory scale using SC-CO<sub>2</sub> include microalgae, peach almond, spent coffee grounds, tomato seed, and wheat germ.<sup>20–24</sup>

The objective of the current study was to extract osage orange oil using SC-CO<sub>2</sub> and to determine fuel properties of the derived osage orange methyl esters (OOMEs). Using standard test methods, the following properties were measured: cold flow, oxidative stability, derived cetane number (DCN), sulfur, free and total glycerol content, kinematic viscosity (KV), acid value (AV), phosphorus, lubricity, peroxide value (PV), density, moisture content, gross heat of combustion, Gardner color, and iodine value (IV). A comparison to ASTM D6751 and EN 14214 was a further objective. Also measured were fuel properties of B5 and B20 blends in ultra-low sulfur (<15 ppm) diesel (ULSD) fuel and a comparison to petrodiesel fuel standards.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Mature osage orange fruits (100–175 mm in diameter) were collected from wild populations in McLean County, IL, in late summer and early fall of 2008 and 2009. A total of 30–50 fruits were soaked in water for 3 weeks using 32 gallon trash cans. During this period, the fruits disintegrated, the flocculate was removed with strainers, and the water was replaced several times. Seeds were collected from the bottom of the cans and washed several times with water using metal mesh strainers (0.06 in. opening) to remove residual fruit material. Seeds were air-dried for 3 days and stored at room temperature until further use. The seeds were then ground in a Retsch GM200 grinder (Glen Mills, Inc., Clifton, NJ). The ground seeds had an average particle size of ca. 1.0 mm and a moisture content of ca. 10.0%.

ULSD was donated by a major petrochemical company. Conductivity and corrosion inhibitor additives were added by the manufacturer, but no drag-reducing, lubricity, cold-flow, or antioxidant additives were present. Fatty acid methyl ester (FAME) standards were purchased from

Nu-Chek Prep, Inc. (Elysian, MN). Tocopherol standards (≥97% purity) were obtained from Matreya, LLC (Pleasant Gap, PA). All other chemicals and reagents were obtained from Sigma-Aldrich Corp. (St. Louis, MO) and used as received.

**2.2. SC Fluid Extraction.** Small-scale SC-CO<sub>2</sub> extractions for quantification of oil content were performed in a Spe-ed SFE unit (Applied Separations, Allentown, PA), essentially in agreement with American Oil Chemists' Society (AOCS) official method Am 3-96. Ground seeds (10 g) were placed in a 24 mL extraction cell and extracted with SC-CO<sub>2</sub> at 80 °C and 55.2 MPa with a flow rate of 3 L of CO<sub>2</sub>/min (expanded gas). The restrictor temperature was 70 °C, and a solvent/feed ratio of 50:1 (g/g) was used. The collected oil was dried under a gentle stream of nitrogen at 70 °C to a constant mass. The oil yield (g of oil/100 g of seeds) was based on the dry mass of the seeds. Four replications were performed.

Large-scale SC-CO<sub>2</sub> extractions were conducted using a pilot-plant extractor previously described.<sup>25</sup> The extraction cells held 1.5 kg of ground osage orange seeds, and the extraction conditions were as follows: 80 °C and 55.2 MPa with a flow rate of 0.3 kg of CO<sub>2</sub>/min. A reduced pressure receiver held at 40 °C and 17.2 MPa was used to collect the extracted oil. The extraction cell was filled twice, and all of the oil was combined. About 127 kg of CO<sub>2</sub> was used to extract 3.0 kg of osage orange seeds for a solvent/feed ratio (g/g) of 42:1. The overall oil yield (g of oil/100 g of seeds) was based on the fresh weight of the seeds. Extracted oil samples were stored at −15 °C until further use.

**2.3. Fatty Acid Profile.** FAMES prepared as described previously<sup>26</sup> were separated using a Varian (Walnut Creek, CA) 8400 gas chromatograph (GC) equipped with a flame ionization detector (FID) and SP2380 (Supelco, Bellefonte, PA) column (30 m × 0.25 mm inner diameter and 0.20 μm film thickness). Carrier gas was He at 1 mL/min. The oven temperature was initially held at 150 °C for 15 min and then increased to 210 °C at 2 °C/min, followed by an increase to 220 °C at 50 °C/min. The injector and detector temperatures were set at 240 and 270 °C, respectively. FAME peaks (triplicates, means reported) were identified by a comparison to the retention times of reference standards.

**2.4. Acid Pretreatment.** Acid-catalyzed pretreatment of crude osage orange oil (AV of 17.89 mg of KOH/g) was conducted in a 1 L three-necked round-bottom flask connected to a reflux condenser and a mechanical magnetic stirrer set to 1200 rpm. Initially, oil and methanol (35 vol %) were added to the flask, followed by dropwise addition of concentrated (18 M) sulfuric acid (1.0 vol %). The contents were heated at reflux for 4 h. After cooling to room temperature, the phases were separated. The oil phase was washed with distilled water until a neutral pH was achieved, followed by rotary evaporation (20 mbar and 30 °C) to remove residual methanol. Finally, drying with magnesium sulfate (MgSO<sub>4</sub>) provided the acid-pretreated oil (AV of 0.33 mg of KOH/g).

**2.5. Transesterification.** Methanolysis of acid-pretreated osage orange oil (400 g) was accomplished with a sodium methoxide catalyst (0.5 mass % with respect to oil), 6:1 mol ratio of methanol (88 g)/oil, 60 °C reaction temperature, and 1.0 h reaction time. After sequential removal of glycerol by gravity separation and methanol by reduced pressure (10 mbar and 30 °C) rotary evaporation, FAMES were washed with distilled water until a neutral pH was obtained and dried with MgSO<sub>4</sub> to yield OOMEs in high yield (95 mass %).

**2.6. Tocopherol Content.** Tocopherols were quantified by high-performance liquid chromatography (HPLC) using a Thermo Separation Products (San Jose, CA) SpectraSYSTEM pump and auto sampler connected by a Starrett column splitter (40:60) to a Surveyor FL Plus fluorescence detector and SpectraSYSTEM UV2000 detector in parallel. Samples (50 mg) were dissolved in hexane (1 mL) and injected (10  $\mu$ L) onto a YMC-Pack Diol-NP (YMC, Wilmington, NC) column (5  $\mu$ m, 250  $\times$  4.6 mm inner diameter). The mobile phase consisted of 97:3 (v/v) hexane/tetrahydrofuran, with a flow rate of 2 mL/min. Tocopherol peaks were identified (triplicates, means reported) by a comparison to the retention times of reference standards. Peak areas from the fluorescence detector (excitation, 292 nm; emission, 344 nm) were used to quantify tocopherols by external calibration with pure standards. The UV detector, set at 295 nm, was used for verification of tocopherol peak identification.

**2.7. Fuel Properties.** Unless stated otherwise, all data were collected according to standard test methods in triplicate with mean values reported. The following properties were measured following AOCS, ASTM, and CEN official methods using instrumentation described previously:<sup>8–10,27,28</sup> AV (mg of KOH/g), ASTM D664; cloud point (CP, °C), ASTM D5773; cold-filter plugging point (CFPP, °C), ASTM D6371; free and total glycerol (mass %, single determinations), ASTM D6584; Gardner color (single determination), AOCS Td 1a-64; gross heat of combustion [higher heating value (HHV), MJ/kg], ASTM D4809; induction period (IP, h), EN 14112 (B100) and EN 15751 (blends); iodine value (IV, g of I<sub>2</sub>/100 g), AOCS Cd 1c-85; Karl Fischer moisture content (ppm), ASTM D6304; kinematic viscosity (KV, mm<sup>2</sup>/s), ASTM D445; lubricity ( $\mu$ m), ASTM D6079; phosphorus (P, mass %), ASTM D4951; pour point (PP, °C), ASTM D5949; density, AOCS Cc 10a-25; sulfur (S, ppm), ASTM D5453; and viscosity index (VI), ASTM D2270. For a greater degree of precision, the PP was measured with a resolution of 1 °C, instead of the specified 3 °C increment. Derived CN (DCN) was determined ( $n = 32$ ) by the Southwest Research Institute (San Antonio, TX) following ASTM D6890 as opposed to the more traditional CN measurement by ASTM D613 because of the smaller sample size requirement of ASTM D6890.

The oxidation onset temperature (OT, °C) was determined by pressurized differential scanning calorimetry (PDSC) using a model Q10P thermal analyzer from TA Instruments (Newcastle, DE). A 2  $\mu$ L sample, resulting in a film thickness of <1 mm, was placed in an aluminum pan hermetically sealed with a pinhole lid and oxidized with pressurized (1.38 MPa; 200 psi) dry air (Gateway Airgas, St. Louis, MO), with a heating rate of 10 °C/min from 50 to 350 °C. A plot of heat flow (W/g) versus temperature (°C) was used to determine OT.

**Table 3. Fatty Acid Composition (Area %) of Osage Orange Seed Oil**

fatty acid <sup>a</sup>	osage orange
C14:0	0.1
C16:0	7.0 (0.6) <sup>b</sup>
C16:1 9c	0.1
C18:0	2.4 (0.1)
C18:1 9c	11.9 (0.2)
C18:1 11c	0.8
C18:2 9c, 12c	76.4 (0.4)
C18:3 9c, 12c, 15c	0.4
C20:0	0.6
unknown (sum)	0.3
$\Sigma$ saturated <sup>c</sup>	10.1
$\Sigma$ monounsaturated <sup>d</sup>	12.8
$\Sigma$ polyunsaturated <sup>e</sup>	76.8

<sup>a</sup> For example, C18:1 9c signifies an 18 carbon fatty acid chain with one *cis* (c) double bond located at carbon 9 (methyl 9Z-octadecenoate; methyl oleate). <sup>b</sup> Values in parentheses are standard deviations. Where not indicated, the value is 0. <sup>c</sup>  $\Sigma$ saturated = C14:0 + C16:0 + C18:0 + C20:0. <sup>d</sup>  $\Sigma$ monounsaturated = C16:1 + C18:1. <sup>e</sup>  $\Sigma$ polyunsaturated = C18:2 + C18:3.

**Table 4. Tocopherol Content (ppm) of Crude Osage Orange Seed Oil and Methyl Esters**

	oil	methyl esters
$\alpha$ -tocopherol	125 (2) <sup>a</sup>	55 (0)
$\beta$ -tocopherol	86 (1)	84 (1)
$\delta$ -tocopherol	185 (2)	187 (2)
$\gamma$ -tocopherol	147 (8)	142 (1)
$\Sigma$ tocopherols <sup>b</sup>	543 (2)	468 (1)

<sup>a</sup> Values in parentheses are standard deviations. <sup>b</sup>  $\Sigma$ tocopherols = total tocopherol content.

The peroxide value (PV, mequiv of peroxide kg<sup>-1</sup>) was determined following the modified ferric thiocyanate method by Shantha and Decker, as described by Hu et al.<sup>29,30</sup> Hydroperoxides were calculated using a standard curve made from solutions of ferric chloride (0–15  $\mu$ g of Fe<sup>3+</sup>).

Measured amounts of OOMEs and ULSD were splash-blended at room temperature in a conical flask with continuous vigorous stirring to ensure uniform mixing. The blends were based on volume with B5 and B20 samples prepared.

### 3. RESULTS AND DISCUSSION

**3.1. Composition and Properties of Osage Orange Oil.** The FA profile and tocopherol content of osage orange oil are given in Tables 3 and 4, respectively. The properties of osage orange seed oil are reported in Table 5. The lipid content of osage orange seeds from small-scale analytical SC-CO<sub>2</sub> extractions was 25.0% on a dry mass basis. The overall yield for the pilot-scale extraction was 20.9% on a fresh weight basis. The principle FA identified in osage orange oil was linoleic acid (76.4%). Oleic (11.9%), palmitic (7.0%), and stearic (2.4%) acids constituted most of the remaining FA profile, with lesser amounts (<1%) of other FAs also detected. The combined polyunsaturated FA content was thus 76.8%, with monounsaturated and saturated FAs



Table 5. Properties of Crude Osage Orange Seed Oil

	crude osage orange oil <sup>a</sup>
oil content (mass %)	25.0
acid value (mg of KOH/g)	17.89 (0.15) <sup>b</sup> /0.33 (0.01)
iodine value (g of I <sub>2</sub> /100 g)	144
cold-flow properties	
PP (°C)	−26.7 (1.2)
oxidative stability	
IP at 110 °C (h)	1.1 (0.1)
OT (°C)	150.5 (1.7)
PV (mequiv/kg)	6.69 (0.05)/4.78 (0.05)
kinematic viscosity	
at 25 °C (mm <sup>2</sup> /s)	54.37 (0.09)
at 40 °C (mm <sup>2</sup> /s)	30.71 (0.08)
at 100 °C (mm <sup>2</sup> /s)	7.39 (0.01)
viscosity index	222
sulfur (ppm)	6/58
phosphorus (mass %)	0.45/0.33
moisture content (ppm)	1944 (32)/522 (3)
wear scar at 60 °C (μm)	118 (4)
density	
at 15.6 °C (kg/m <sup>3</sup> )	929 (1)
at 40 °C (kg/m <sup>3</sup> )	912 (1)
Gardner color	7

<sup>a</sup>Where two values are indicated, the first represents data for crude oil and the second represents data from acid-pretreated oil. <sup>b</sup>Values in parentheses are standard deviations. For the iodine value, sulfur, and phosphorus, *n* = 1.

comprising 12.8 and 10.1%, respectively, of the overall FA content of osage orange oil. Similar results were reported previously.<sup>12</sup> The FA profile of osage orange oil closely approximated that of safflower oil.<sup>31</sup> Although not investigated here, applications such as a non-yellowing drying oil and as a starting material for the preparation of conjugated C18:2 FAs may be applicable to osage orange oil, as safflower has found similar utility as a result of its FA composition.<sup>31</sup>

The primary tocopherol identified in crude osage orange oil was the  $\delta$  homologue (185 ppm), with progressively lower concentrations of  $\gamma$ -,  $\alpha$ -, and  $\beta$ -tocopherols (147, 125, and 86 ppm, respectively) also detected. The combined endogenous content was thus 543 ppm, which was lower than the typical amount observed in oils from corn, cottonseed, palm, sesame, soybean, and sunflower.<sup>32</sup> In addition,  $\gamma$ -tocopherol is generally the principle homologue identified in corn, linseed, rapeseed, sesame, and soybean oils, with  $\alpha$ -tocopherol found in greatest quantity in cottonseed, olive, palm, and sunflower oils.<sup>32</sup>

The AV of crude osage orange oil was measured as 17.89 mg of KOH/g. The iodine value was calculated from the FA profile and found to be 144 g of I<sub>2</sub>/100 g. The Gardner color of the crude oil was 7 (1 is lightest, and 18 is darkest). Cold-flow properties were determined by measurement of PP, and a value of −26.7 °C was obtained. Because CP is an optical method and requires translucent samples for determination, it was not measured as a result of the opacity of crude osage orange oil. Oxidative stability was quantified by Rancimat (EN 14112) and PDSC methods through measurement of IP (1.1 h; EN 14112) and OT (150.5 °C; PDSC). KV was determined at 25, 40, and 100 °C and yielded results of 54.37, 30.71, and 7.39 mm<sup>2</sup>/s, respectively.

The calculated VI was thus found to be 222. Densities of 929 and 912 kg/m<sup>3</sup> were obtained at 15.6 and 40 °C, respectively. As expected, the density and KV decreased with an increasing temperature. The wear scar generated by the high-frequency reciprocating rig (HFRR) lubricity method (ASTM D6079, 60 °C) was 118 μm.

Mineral acid-catalyzed pretreatment was performed on the crude oil to render it amenable to transesterification by a homogeneous alkali base. The influence of pretreatment on selected properties of the oil was determined. As expected, a considerably lower AV (0.33 mg of KOH/g) was obtained after esterification of free fatty acids (FFAs) during pretreatment. Because a sulfur-containing acid (H<sub>2</sub>SO<sub>4</sub>) was used during pretreatment, an increase in sulfur content from 6 to 68 ppm was observed. The content of phosphorus remained relatively constant, with values of 0.45 and 0.33 mass % detected before and after pretreatment, respectively. The moisture content was reduced considerably upon pretreatment, as evidenced by values of 1944 (before) and 522 (after) ppm. Such a result was not surprising, because a drying step was performed at the conclusion of the acid pretreatment procedure. The extent of autooxidation was quantified by PV. Higher PVs are indicative of greater oxidative degradation before a maximum PV is reached. After the maximum, PV decreases because peroxide intermediates are further decomposed to other oxygenated species.<sup>29</sup> The initial PV of crude osage orange oil was 6.69 mequiv of peroxides/kg. After pretreatment, a PV of 4.78 mequiv of peroxides/kg was obtained. Presumably, the conditions of pretreatment were sufficient to decompose at least a portion of the peroxides, thus resulting in a lower PV.

**3.2. Preparation and Quality of OOMEs.** Previous studies determined that FFA contents greater than 0.50 wt % (AV of 1.0 mg of KOH/g) were detrimental to the yield of FAMES produced by homogeneous alkali-catalyzed transesterification.<sup>33,34</sup> FFAs react with alkali bases, such as sodium methoxide, to form undesirable soap (sodium salt of FA) and methanol (or water in the case of sodium hydroxide), thus irreversibly quenching the catalyst and reducing FAME yield.<sup>2,35</sup> Consequently, acid pretreatment was performed prior to methanolysis to reduce the FFA content of osage orange oil. Homogeneous alkali-catalyzed (sodium methoxide) transesterification afforded OOMEs in high yield (95 mass %), employing classic reaction conditions described previously.<sup>2,8,10,27,36</sup> Optimization of the OOME yield using statistical techniques, such as response surface methodology, was considered beyond the scope of the current study.

The quality of OOMEs was verified by the determination of free and total glycerol content along with AV. Both ASTM D6751 and EN 14214 specify maximum permissible limits for free and total glycerol in biodiesel (Table 1). As seen in Table 1, the free and total glycerol contents of OOMEs were significantly below the prescribed maximum thresholds. Furthermore, a maximum limit of 0.50 mg of KOH/g is specified in ASTM D6751 and EN 14214 for AV. A value of 0.11 mg of KOH/g was obtained for OOMEs, which was significantly below the maximum limit specified in the biodiesel standards.

The preparation of OOMEs resulted in a reduction in the tocopherol content of 14% (Table 4), because the combined amount after methanolysis was lowered to 468 ppm. Retention of the majority of the tocopherol content was not surprising, because they are nonpolar and should partition into hydrophobic materials, such as biodiesel, during purification. Previous studies

also reported that tocopherol content was largely retained after transesterification.<sup>8,27,28,37</sup>

**3.3. Fuel Properties of OOMEs.** The fuel properties of OOMEs along with a comparison to the biodiesel standards are given in Table 1. The Rancimat method (EN 14112) is listed as the oxidative stability specification in ASTM D6751 and EN 14214. A minimum IP (110 °C) of 3 h is required for ASTM D6751, whereas a more stringent limit of 6 h or greater is specified in EN 14214. The IP of OOMEs satisfied neither specification, with a value of 2.4 h. However, the addition of the common synthetic antioxidant *tert*-butylhydroquinone (TBHQ) improved the resistance to oxidation of OOMEs, as evidenced by IPs of 4.1 (250 ppm TBHQ) and 6.4 (500 ppm TBHQ) h. A comparison to the biodiesel standards revealed that, at the higher treatment level (500 ppm TBHQ), OOMEs afforded an IP compliant with both ASTM D6751 and EN 14214. The poor oxidative stability of OOMEs was attributed to its high content of polyunsaturated FAMES. The rate of autooxidation of FAMES depends upon the presence of methylene positions allylic to double bonds, with bis-allylic methylene positions even more susceptible to oxidation. As a result, polyunsaturated FAMES are particularly vulnerable to autooxidation, as evidenced by the relative rates of oxidation of the unsaturated ethyl esters of oleic, linoleic, and linolenic acids: 1, 41, and 98.<sup>38</sup> Furthermore, the IPs of FAMES from oleic, linoleic, and linolenic acids were reported as 2.5, 1.0, and 0.2 h, respectively.<sup>39</sup> As discussed previously, linoleic acid was the principle FA detected in osage orange oil.

The OT obtained by PDSC of OOMEs (0 ppm TBHQ) was 164.9 °C. The OT is defined as the temperature at which a rapid increase in the rate of oxidation is observed at constant pressure (1.38 MPa). Higher OTs indicate greater stability to oxidation. For comparison, an OT of 171.6 °C was obtained in a previous study for FAMES prepared from soybean oil.<sup>37</sup>

The PV of OOMEs was 9.82 mequiv of peroxides/kg, which was higher than that obtained for the acid-pretreated oil. Apparently, the conditions of the transesterification reaction or perhaps the purification procedure resulted in the generation of additional peroxides. Presumably, if the PV of OOMEs was lower, higher values for IP and OT would have been obtained, because a value of 9.82 mequiv of peroxides/kg is indicative of at least a small amount of autooxidation having already occurred prior to oxidative stability testing.

As seen in Table 1, OOMEs provided CP, CFPP, and PP values of 3.8, −8.7, and −12.0 °C, respectively. A principal disadvantage of biodiesel versus petrodiesel is inferior cold-flow properties, which is typically exacerbated by the presence of higher melting C16 and C18 saturated FAMES in biodiesel. The CFPP and PP values for OOMEs were lower than the corresponding values obtained for FAMES prepared from soybean, canola, sunflower, and palm oils in a previous investigation.<sup>40</sup> However, the CP of OOMEs was similar to CPs reported for soybean- and sunflower-based FAMES.<sup>40</sup> The saturated FAME content of OOMEs was not significantly different from that of soybean- (14.6%) and sunflower-based (9.8%) FAMES reported previously.<sup>40</sup> The content of longer chain (C16+) saturated FAMES along with other high-melting constituents is the most significant factor influencing the CP of biodiesel.<sup>2</sup> The Gardner color of OOMEs was 5, which was lower than what was obtained for the crude oil and higher than what is typically observed for biodiesel prepared from refined oils.<sup>28</sup>

The KV of OOMEs (4.40 mm<sup>2</sup>/s) was within the specified ranges in ASTM D6751 (1.9–6.0 mm<sup>2</sup>/s) and EN 14214

(3.5–5.0 mm<sup>2</sup>/s) at 40 °C. ASTM D6751 does not prescribe limits on density, but EN 14214 specifies a range of 860–900 kg/m<sup>3</sup> (15.6 °C). As seen in Table 1, OOMEs exhibited a value within the specified range in EN 14214 of 892 kg/m<sup>3</sup> at 15.6 °C. Also measured was density at 40 °C, which, as expected, provided a lower value of 890 kg/m<sup>3</sup>.

The DCN of OOMEs (44.9; Table 1) was below the minimum limits of 47 and 51 specified in ASTM D6751 and EN 14214, respectively. However, the DCN value obtained for OOMEs was still in excess of the minimum limit specified in the petrodiesel standards (Table 2). Results generated by ASTM D6890 (DCN) generally correlate with CN determination by ASTM D613. The ASTM D6890 method is now approved as an alternative to the more traditional CN method (ASTM D613) specified in ASTM D6751.<sup>1</sup> Structural factors that influence DCN primarily include the degree of unsaturation and chain length, with higher DCNs observed for FAMES with less unsaturation and longer chain lengths.<sup>2</sup> The high percentage of methyl linoleate was responsible for the low DCN of OOMEs, because methyl linoleate has a reported DCN of 38.2.<sup>41</sup> For comparison, the DCNs of methyl stearate and methyl oleate were reported as 101.0 and 59.3.<sup>41</sup>

The sulfur content of OOMEs was 6 ppm, which was below the specified maximum allowable limits in ASTM D6751 and EN 14214 of 15 and 10 ppm, respectively. In addition, the phosphorus content is limited in ASTM D6751 and EN 14214 to maximum values of 0.001 and 0.0004 mass %, respectively. No phosphorus was detected in OOMEs. Lastly, dissolved water is restricted to a maximum value of 500 ppm in EN 14214. The moisture content of OOMEs was 478 ppm, which was within the prescribed limit and considerably less than what was measured in the crude oil prior to acid pretreatment and transesterification.

ASTM D6751 does not contain an IV specification, but EN 14214 limits IV to a maximum value of 120 g of I<sub>2</sub>/100 g. The IV of OOMEs (144 g of I<sub>2</sub>/100 g) was above the maximum limit prescribed in EN 14214. The high content of polyunsaturated FAMES and methyl linoleate in particular was responsible for the high IV of OOMEs. Blending low-IV FAMES with biodiesel that has an unacceptably high IV is a method by which IV may be lowered.<sup>28,40</sup>

Lubricity (ASTM D6079) is not specified in ASTM D6751 or EN 14214 but is included in the petrodiesel standards ASTM D975, ASTM D7467, and EN 590, with maximum wear scars (60 °C) of 520, 520, and 460 μm prescribed, respectively. The wear scar generated by OOMEs according to ASTM D6079 (HFRR, 60 °C) was 155 μm. As expected, the lubricity of OOMEs was considerably below the maximum limits listed in the petrodiesel standards, which was in agreement with several previous studies indicating that biodiesel possessed inherently good lubricity.<sup>8–10,27,28,37,40,42–44</sup>

Heat of combustion, which affects fuel consumption, is not specified in either ASTM D6751 or EN 14214, but a minimum value of 35 MJ/mg is specified in the European heating oil standard EN 14213. The gross heat of combustion (HHV) of OOMEs was determined by bomb calorimetry (ASTM D4809) to be 39.47 MJ/kg. Such a value is typical for biodiesel fuels but lower than the energy content of petrodiesel.<sup>10,28,44</sup>

A comparison of the fuel properties of OOMEs to that of soybean oil methyl esters (SMEs), the dominant oilseed-derived biodiesel fuel produced in the U.S., revealed several similarities.<sup>10,27,37,40,42,45</sup> Previous studies indicated that SMEs (IV of 124–132 g of I<sub>2</sub>/100 g), similar to OOMEs, exhibited IV and IP data not within the specifications of EN 14214.

Additionally, reported data for HHV, KV, and lubricity for SMEs were similar to OOMEs. However, the DCN of SMEs was within the specifications of the biodiesel standards whereas the value for OOMEs was not. Lastly, PP and CFPP values for SMEs were higher than for OOMEs, although OOMEs exhibited a higher CP. In summary, the fuel properties of OOMEs did not differ significantly in most cases from those of SMEs, thus indicating the acceptability of OOMEs as a source of biodiesel fuel.

**3.4. Blends of OOMEs in Petrodiesel.** The fuel properties of B5 and B20 blends of OOMEs in ULSD along with a comparison to the petrodiesel standards are presented in Table 2. Fuel properties determined in the current study that were affected by blending included AV, moisture content, cold-flow properties, oxidative stability, KV, sulfur content, lubricity, density, and heat of combustion.

The biodiesel–petrodiesel blend standard (B6–B20), ASTM D7467, limits AV to a maximum value of 0.30 mg of KOH/g. The petrodiesel standards ASTM D975 (B0–B5) and EN 590 (B0–B7), however, do not contain AV specifications. The AV of the B20 blend of OOMEs (0.01 mg of KOH/g) was within the range specified in ASTM D7467. The B5 blend also exhibited an AV of 0.01 mg of KOH/g as a result of the low AVs of OOMEs and ULSD (B0).

Dissolved water is limited in EN 590 to a maximum level of 200 ppm. As the percentage of OOMEs in ULSD increased from B0 to B20, the content of moisture increased linearly ( $R^2 = 0.985$ ; figure not shown) from 17 ppm (B0) to 22 ppm (B5) and 55 ppm (B20) as a result of the dissolved content detected in OOMEs. All values were below the maximum threshold listed in EN 590, although the B20 sample contained too much OOMEs to be covered by EN 590.

As mentioned previously, biodiesel is generally inferior to ULSD with regard to cold-flow properties. Illustrative of this is a comparison of neat ULSD (CP,  $-17.5\text{ }^\circ\text{C}$ ; PP,  $-24.0\text{ }^\circ\text{C}$ ; CFPP,  $-18.0\text{ }^\circ\text{C}$ ; Table 2) to OOMEs listed in Table 1. Consequently, blends of OOMEs displayed higher CP values as the percentage of biodiesel was increased from 0 to 20 vol %, although PP up to the B5 level and CFPP were essentially unaffected (Table 2). The responses of CP and PP to the OOME content were nonlinear. With regard to CP, a sharp increase was noted between B0 and B5 but a less dramatic increase was observed between B6 and B20. Neither ASTM D975, ASTM D7467, nor EN 590 specify specific limits on low-temperature operability. Instead, only guidance is provided in the cases of ASTM D975 and ASTM D7467.

Biodiesel was considerably less stable to oxidation than ULSD, as evidenced by an IP of 40.1 h for ULSD. Consequently, blends of OOMEs in ULSD exhibited progressively lower IPs as the percentage of biodiesel was increased from 0 to 20 vol %. The response of IP to the OOME content was nonlinear, because a relatively small increase in the OOME content to the B5 level resulted in a significant reduction of IP. The reduction in IP from B5 to B20 was less pronounced, thus exhibiting a behavior indicative of an exponential relationship between IP and the OOME concentration. The petrodiesel–biodiesel blend standard, ASTM D7467, specifies a minimum IP of 6.0 h. As seen in Table 2, the B20 blend failed to meet this requirement (5.7 h). The B5 blend exhibited an IP of 11.9 h, which was below the minimum value of 20.0 h specified in EN 590. Accordingly, TBHQ was employed at a treatment level of 500 ppm to improve the IPs of the B5 (43.5 h) and B20 (17.3 h) blends to values compliant with EN 590 and ASTM D7467, respectively. The

American petrodiesel standard, ASTM D975, does not contain an oxidative stability specification. The primary reason for the superior oxidative stability of ULSD versus OOMEs was the absence of double bonds and susceptible allylic methylene positions in the case of ULSD. Petrodiesel is principally composed of saturated and aromatic hydrocarbons, which are considerably less susceptible to oxidation than unsaturated FAMES.

Petrodiesel was less viscous than biodiesel, as evidenced by the KV ( $40\text{ }^\circ\text{C}$ ) of ULSD ( $2.30\text{ mm}^2/\text{s}$ ) versus OOMEs ( $4.40\text{ mm}^2/\text{s}$ ). As a result, blends of OOMEs in ULSD afforded progressively higher KVs as the percentage of biodiesel was increased from 0 to 20 vol %. Specifically, the B5 and B20 blends provided values of 2.34 and  $2.57\text{ mm}^2/\text{s}$ , respectively. All of the blends exhibited KVs that were within the ranges specified in the petrodiesel (ASTM D975 and EN 590) and petrodiesel–biodiesel blend (ASTM D7467) standards. The response of KV to the OOME content was highly linear ( $R^2 = 0.989$ ; figure not shown).

As previously stated, petrodiesel (untreated with lubricity-enhancing additives) is inferior to biodiesel with regard to lubricity. In fact, the wear scar generated by ULSD ( $571\text{ }\mu\text{m}$ ) was significantly longer than OOMEs ( $155\text{ }\mu\text{m}$ ) and in excess of the maximum allowable wear scar lengths specified in ASTM D6751, ASTM D7467, and EN 590. Accordingly, blends of OOMEs in ULSD exhibited progressively better lubricities (shorter wear scars) as the percentage of biodiesel was increased from 0 to 20 vol %. The response of lubricity to the OOME content was nonlinear, because a small increase in the OOME content resulted in a substantial reduction in the wear scar length. The effect diminished when the percentage of OOMEs increased beyond the B5 level. In fact, even at the B5 blend level, the blend was well within the limits listed in the aforementioned petrodiesel standards (ASTM D975 and EN 590), providing a wear scar of  $233\text{ }\mu\text{m}$ . The B20 blend afforded an even shorter wear scar of  $160\text{ }\mu\text{m}$ , which was well below the maximum threshold specified in ASTM D7467. As was the case in prior studies, biodiesel (OOMEs) proved to be an excellent lubricity additive for ULSD.<sup>8–10,27,28,37,40,42–44</sup>

Density at  $15.6\text{ }^\circ\text{C}$  is limited in EN 590 to a range of  $820\text{--}845\text{ kg/m}^3$ . As the percentage of OOMEs in ULSD increased from B0 to B20, density ( $15.6\text{ }^\circ\text{C}$ ) increased linearly ( $R^2 = 0.980$ ; figure not shown) from  $837\text{ kg/m}^3$  (B0) to  $839\text{ kg/m}^3$  (B5) and  $855\text{ kg/m}^3$  (B20) as a result of the higher density of OOMEs. The values obtained for the B0 and B5 blends were below the maximum threshold listed in EN 590, but the B20 blend was above the limit. However, the B20 sample contained too much OOMEs to be covered by EN 590. Neither ASTM D975 nor D7467 specify limits for density. Also collected was density at  $40\text{ }^\circ\text{C}$ , and as expected, lower densities were observed at this temperature than at  $15.6\text{ }^\circ\text{C}$ .

The sulfur content is limited in the American petrodiesel standards, ASTM D975 and ASTM D7467, to a maximum value of 15 ppm, whereas a more stringent limit of 10 ppm is prescribed in EN 590. As the content of OOMEs increased from B0 to B20, the sulfur content decreased linearly ( $R^2 = 0.923$ ; figure not shown) from  $9\text{ kg/m}^3$  (B0) to  $8\text{ kg/m}^3$  (B5) and  $7\text{ kg/m}^3$  (B20) as a result of the lower sulfur content of OOMEs. All samples were below the maximum prescribed limits for sulfur contained in the petrodiesel standards.

Petrodiesel contained greater energy content than biodiesel, as evidenced by a HHV for ULSD of  $46.23\text{ MJ/kg}$  versus  $39.47\text{ MJ/kg}$  for OOMEs. As a result, blends of OOMEs in ULSD afforded progressively lower HHVs as the percentage of biodiesel was



increased from 0 to 20 vol %. A linear relationship ( $R^2 = 0.905$ ; figure not shown) was noted between HHV and the OOME content. Specifically, the B5 and B20 blends provided values of 45.18 and 44.24 MJ/kg, respectively. Hydrocarbon components of ULSD generally have greater energy content than FAMES, in part because hydrocarbons do not contain oxygen. Because combustion is an oxidative process, FAMES are in effect initially more oxidized than hydrocarbons as a result of the presence of chemically bound oxygen, which results in lower energy contents when expressed as MJ/kg.<sup>44</sup> None of the petrodiesel standards specifies limits for HHV.

#### 4. CONCLUSIONS

Biodiesel was prepared in high yield by homogeneous alkali-catalyzed transesterification after acid pretreatment of SC-CO<sub>2</sub>-extracted osage orange seed oil. Fuel properties, such as AV, CP, CFPP, PP, DCN, IP, IV, KV, OT, PV, density, energy content, Gardner color, glycerol content, lubricity, moisture content, and sulfur and phosphorus contents, were determined. In addition, B5 and B20 blends of OOMEs in ULSD were prepared and evaluated against the petrodiesel standards ASTM D975, ASTM D7467, and EN 590. Lastly, the composition and properties of crude osage orange oil were discussed.

The principle component identified in OOMEs was methyl linoleate at 76.4%, which explained several fuel properties. As a result of the relatively high content of unsaturated FAMES, such as methyl linoleate, OOMEs exhibited DCN and IP values below the limits specified in the biodiesel standards. The addition of TBHQ at 500 ppm was required to provide an IP compliant with both ASTM D6751 and EN 14214. In addition, the IV of OOMEs was in excess of the maximum limit specified in EN 14214 as a result of the high methyl linoleate content. Blending with feedstocks containing higher percentages of saturated FAMES would presumably ameliorate the high IV as well as the low DCN and IP of OOMEs. The AV, glycerol content, KV, moisture content, phosphorus content, and sulfur content of OOMEs were within the limits prescribed in ASTM D6751 and EN 14214. In addition, OOMEs exhibited data for density, lubricity, and energy content that was typical of biodiesel fuels. Lastly, the CFPP and PP values for OOMEs were superior to those reported for several more common biodiesel fuels, such as FAMES, prepared from canola, soybean, palm, and sunflower oils.

Blends of OOMEs in ULSD yielded AVs, KVs, moisture contents, sulfur contents, lubricities, and densities within the limits prescribed in the petrodiesel standards ASTM D975, ASTM D7467, and EN 590. Furthermore, the cold-flow properties of the blends, although less favorable than neat ULSD, were comparable to data for blends reported elsewhere. Lastly, the addition of TBHQ at a level of 500 ppm provided IPs compliant with the specifications contained in EN 590 and ASTM D7467 for the B5 and B20 blends, respectively. Linear responses were noted between the OOME concentration and moisture content, KV, sulfur content, density, and energy content. Nonlinear relationships were elucidated for CP, PP, CFPP, IP, and lubricity.

On the basis of the data reported herein, OOMEs represent an acceptable substitute or blend component for petrodiesel, because OOMEs compared favorably to most biodiesel and petrodiesel fuel specifications. In addition, the fuel properties of OOMEs did not differ significantly in most cases from those of SMEs, thus further indicating the acceptability of OOMEs as a

potential source of biodiesel fuel. In some cases, additives or blending were required to satisfy fuel specifications, but these strategies are ubiquitous in the fuel industry. In summary, osage orange seeds provide a low-cost, non-food, high-oil-producing feedstock suitable for production of biodiesel.

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#### DISCLOSURE

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