

Evaluation of Castor and Lesquerella Oil Derivatives as Additives in Biodiesel and Ultralow Sulfur Diesel Fuels[†]

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The use of petroleum-derived additives is ubiquitous in fuels production, including biodiesel (BD) and ultralow sulfur diesel (ULSD) fuels. Development and employment of domestically derived, biodegradable, renewable, and nontoxic additives is an attractive goal. As such, estolides (**1**, **2**) and 2-ethylhexyl esters (**3**, **4**) derived from castor and lesquerella oils, due to their excellent low temperature, lubrication, and oxidation stability properties, were investigated as potential fuel additives in soybean oil methyl esters (SME), palm oil methyl esters (PME), and ULSD. With respect to SME and PME, low temperature operability improvement utilizing **1–4** at low blend ratios (≤ 5 wt %) was of interest. Although **1–4** did not affect the cloud point (CP) or pour point (PP) of SME, the PP of PME was improved by 3 °C, indicating that **1–4** may be useful as pour point depressants for PME in moderate temperature climates. With respect to ULSD, improvement of lubricity employing **1–4** was of interest. All materials imparted significantly improved lubricity to ULSD at low blend ratios (≤ 2 wt %). In fact, **3** and **4** were superior to SME and PME as lubricity enhancers in ULSD. Estolides **1** and **2** imparted superior lubricity to ULSD when compared to PME. These results indicate that **1–4** would be as or more effective lubricity enhancers in ULSD than SME and PME. Kinematic viscosity of blends of **1–4** in SME, PME, and ULSD tended to increase with increasing level of additive, but all values were within prescribed relevant kinematic viscosity fuel specifications. In summary, biobased materials, such as **1–4**, have potential as fuel additives in BD and ULSD.

1. Introduction

Biodiesel (BD), defined as fatty acid methyl esters (FAME) derived from methanolysis of vegetable oil, animal fat, or waste oil, is an attractive and environmentally friendly alternative to petrodiesel for combustion in compression-ignition (diesel) engines. BD has attracted considerable interest recently because it is biodegradable, renewable, produced domestically, and nontoxic.^{1,2} Moreover, BD exhibits improved lubricity, higher flash point, reduced overall exhaust emissions, and similar viscosity, cetane number, and gross heat of combustion in comparison to petrodiesel.^{2–5} However, BD is still faced with technical challenges, such as oxidation stability, low temperature operability, and nitrogen oxides (NOx) exhaust emissions.¹ The employment of additives originally developed for petrodiesel is a common strategy to address one or more of the technical deficiencies of BD; however, few petrodiesel additives are effective in BD. Therefore, development of new additives

specifically for use in BD that are domestically derived, biodegradable, nontoxic, and renewable is an attractive research goal.^{6,7}

Ultralow sulfur diesel fuel (ULSD, ≤ 15 ppm S) is currently mandated for on-highway use by the United States Federal Government. However, hydrosulfurization negatively affects the lubricity and low temperature performance of petrodiesel by reducing the oxygen, nitrogen, aromatic, and olefinic content of ULSD.^{8–10} Consequently, the petroleum industry adds proprietary additives to ULSD to satisfy the ASTM D975¹¹ diesel fuel standard. Although the exact nature of petrodiesel additives is a closely guarded secret, they are generally derived from petrochemical materials. As such, the development of new additives for use in ULSD that are environmentally friendly, renewable, and of a domestic origin is once again a desirable goal.

Estolides are synthetic, biodegradable, nontoxic, renewable, vegetable oil-based, functional fluids that are produced when the carboxylic acid moiety of one fatty acid is reacted at a site of unsaturation of another fatty acid to form a secondary ester linkage.^{12–14} Estolides have excellent low temperature, oxidation

[†] Disclaimer: Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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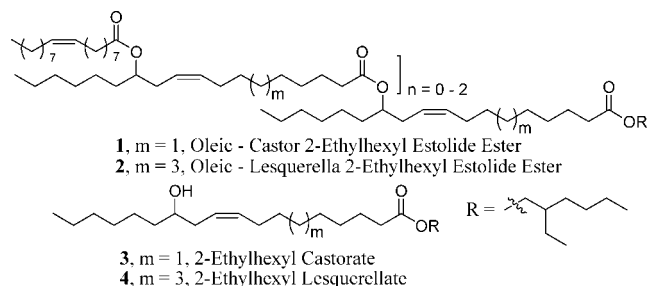


Figure 1. Estolides **1** and **2** and 2-ethylhexyl esters of castor (**3**) and lesquerella (**4**) oils.

Table 1. Selected Biodiesel and ULSD Fuel Specifications

	biodiesel		ULSD
	ASTM D6751	EN 14214	ASTM D975
ν , mm ² /s, 40 °C	1.9–6.0	3.5–5.0	1.9–4.1
CP, °C	report		depends ^a
PP, °C			depends ^a
lubricity, μ m			520 max

^a On location.

stability, and lubrication properties, which makes them attractive as potential components in coatings, cosmetics, greases, inks, lubricants, plastics, and surfactants.^{13–15} Estolides with oleic acid capping units based on castor (**1**, Figure 1) and lesquerella (**2**, Figure 1) oils, along with 2-ethylhexyl esters of castor (**3**, Figure 1) and lesquerella (**4**, Figure 1) oils, exhibit properties significantly improved over the parent vegetable oils.¹⁵ Therefore, the objective of the current study was to determine the effect of **1–4** at additive levels on relevant fuel properties of BD and ULSD (Table 1). Of particular interest was the effect of **1–4** on the low temperature performance of BD and lubricity of ULSD. The effect of soybean oil methyl esters (SME) and palm oil methyl esters (PME) on selected fuel properties of ULSD was also determined and compared to **1–4**.

2. Experimental Section

2.1. Materials. SME was obtained from the Stepan Company (Northfield, IL), and PME, from the Malaysian Palm Oil Board (Selangor, Malaysia). ULSD, described as fungible by the manufacturer, was gifted direct from the refiner without additives from a major multinational petrochemical company that wishes to remain anonymous. All other chemicals and reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI). All materials were used as received.

2.2. Equipment. Fatty acid methyl esters (FAME) in SME and PME were separated using a Varian (Walnut Creek, CA) 8400 GC equipped with a flame ionization detector and SP2380 (Supelco, Bellefonte, PA) column (30 m \times 0.25 mm i.d., 0.20 μ m film thickness). The carrier gas was He at 1 mL/min. The oven temperature was initially held at 150 °C for 15 min, then increased to 210 at 2 °C/min, followed by an increase to 220 at 50 °C/min. The injector and detector temperatures were set at 240 and 270 °C, respectively. FAME peaks (Table 2) were identified by comparison to the retention times of known reference standards.

Cloud point (CP, °C) and pour point (PP, °C) determinations were made in agreement with ASTM D5773¹⁶ and ASTM D5949,¹⁷

Table 2. Fatty Ester Profiles of SME and PME

FAME	SME	PME
C12:0		0.2
C14:0	0.1	1.2
C16:0	10.9	46.1
C18:0	4.5	4.4
C20:0	0.2	0.2
C22:0	0.1	0.1
C18:1	22.4	37.8
C18:2	53.1	9.4
C18:3	7.2	0.1
other	1.5	0.5

Table 3. Fuel Properties of Neat Materials

	CP (°C)	PP (°C)	ν (mm ² /s)	HFRF (μ m)
caster estolide 1	−45	−54	36.24	180
lesquerella estolide 2	−35	−48	26.56	133
caster ester 3	−27	−33	22.03	201
lesquerella ester 4	−25	−27	15.41	161
SME	1	0	4.13	162
PME	>rt	18	4.54	172
soybean oil	−5	−6	23.30	182
palm oil	>rt	>rt	nd ^a	195
ULSD	−12	−21	2.32	551

^a nd: not determined.

Table 4. Evaluation of **1–4** in SME and PME

SME				PME			
wt %	CP (°C)	PP (°C)	ν (mm ² /s)	wt %	CP (°C)	PP (°C)	ν (mm ² /s)
0	1	0	4.13	0	>rt	18	4.54
0.1 1	1	0	4.15	0.1 1	>rt	18	4.54
0.5 1	1	0	4.18	0.5 1	>rt	17	4.59
1.0 1	1	0	4.21	1.0 1	>rt	16	4.66
2.0 1	1	0	4.29	2.0 1	>rt	16	4.78
5.0 1	1	0	4.53	5.0 1	>rt	15	4.96
0.1 2	1	0	4.14	0.1 2	>rt	18	4.54
0.5 2	1	0	4.18	0.5 2	>rt	17	4.57
1.0 2	1	0	4.19	1.0 2	>rt	16	4.62
2.0 2	1	0	4.24	2.0 2	>rt	16	4.75
5.0 2	1	0	4.43	5.0 2	>rt	15	4.93
0.1 3	1	0	4.14	0.1 3	>rt	18	4.54
0.5 3	1	0	4.16	0.5 3	>rt	17	4.56
1.0 3	1	0	4.19	1.0 3	>rt	16	4.61
2.0 3	1	−1	4.23	2.0 3	>rt	15	4.71
5.0 3	1	−1	4.37	5.0 3	>rt	15	4.91
0.1 4	1	0	4.14	0.1 4	>rt	18	4.54
0.5 4	1	0	4.15	0.5 4	>rt	17	4.55
1.0 4	1	0	4.17	1.0 4	>rt	16	4.61
2.0 4	1	−1	4.21	2.0 4	>rt	15	4.68
5.0 4	1	−1	4.29	5.0 4	>rt	15	4.87

respectively, using a Phase Technology Analyzer Model PSA-70S (Richmond, B.C., Canada). Each sample was run in triplicate and average values rounded to the nearest whole degree (± 1 °C) are reported (Tables 3–5). For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment.

Lubricity determinations were made at 60 °C (controlled to less than ± 1 °C), according to ASTM D6079¹⁸ using a PCS Instruments (London, UK) Model HFRHCA8 high frequency reciprocating rig (HFRF) lubricity tester. At the conclusion of each test, the ball was visually inspected for wear and the dimensions of an observed wear scar (μ m) were averaged. All wear scar data (Tables 3 and 5) are the averages of two replicates.

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Table 5. Evaluation of 1–4, SME, and PME in ULSD

wt %	CP (°C)	PP (°C)	ν (mm ² /s)	HFRR (μ m)
0	−12	−21	2.32	551
0.1 1	−12	−22	2.61	399
0.5 1	−12	−22	2.63	311
1.0 1	−12	−23	2.66	272
2.0 1	−12	−23	2.68	243
0.1 2	−12	−22	2.35	349
0.5 2	−12	−22	2.39	306
1.0 2	−12	−22	2.44	270
2.0 2	−12	−23	2.45	208
0.1 3	−12	−22	2.56	393
0.5 3	−12	−22	2.58	267
1.0 3	−12	−22	2.61	189
2.0 3	−12	−22	2.63	180
0.1 4	−12	−22	2.53	420
0.5 4	−12	−22	2.57	312
1.0 4	−12	−22	2.59	198
2.0 4	−12	−22	2.65	188
0.1 SME	−12	−22	2.38	394
0.5 SME	−12	−22	2.38	348
1.0 SME	−12	−22	2.40	235
2.0 SME	−12	−21	2.48	212
5.0 SME	−12	−21	2.57	180
20.0 SME	−10	−16	2.71	171
0.1 PME	−12	−23	2.47	413
0.5 PME	−12	−22	2.59	386
1.0 PME	−12	−22	2.60	381
2.0 PME	−12	−21	2.67	349
5.0 PME	−11	−18	2.71	210
20.0 PME	−8	−12	2.85	172

Kinematic viscosity (ν , mm²/s, 40 °C) was determined following ASTM D7042¹⁹ using an Anton Paar Stabinger Viscometer model SVM3000 (Ashland, VA). Each sample was run in triplicate, and average values are reported (Table 3–5).

2.3. Preparation of 1–4. The synthesis of estolides **1** and **2** and esters **3** and **4** was performed as described previously.¹⁵ The structure and purity of the products were verified through spectroscopic and physical property comparison with authentic previously prepared samples.

3. Results and Discussion

3.1. Effect of 1–4 on SME and PME. The inferior low temperature performance of BD in comparison to ULSD, especially in subambient conditions, has been widely reported, both in scientific and nontechnical literature. Consequently, development of cold flow improver (CFI) additives for use in BD has attracted considerable scientific interest. Estolides **1** and **2** (Figure 1), which have excellent low temperature properties (Table 3), were investigated as potential CFI additives in SME and PME. Moreover, 2-ethylhexyl esters of castor (**3**) and lesquerella (**4**) oils, which also have superior cold flow characteristics, were also explored as prospective CFI additives. Because **1–4** exhibit significantly higher kinematic viscosities (40 °C) than typical BD fuels, this parameter was also monitored in an effort to remain within ASTM D6751 and EN 14214 biodiesel kinematic viscosity specifications (Table 1). As a result, 5 wt % was chosen as the maximum blend ratio of **1–4** in SME and PME in an effort to remain within the specified kinematic viscosity limits. As indicated by Table 4, **1–4** had little, if any, impact on the CP and PP of SME. Also shown in Table 4, **1–4** had no effect on the CP of PME, but its PP was improved (3 °C in all cases). As expected, with increasing percentage of **1–4** in either SME or PME, an increase in

kinematic viscosity was observed. However, all samples remained within the aforementioned kinematic viscosity specifications.

3.2. Effect of 1–4 on ULSD. The utilization of ULSD in the United States has necessitated further development of lubricity enhancing additives to satisfy ASTM D975 (520 μ m maximum wear scar length by HFRR at 60 °C, Table 1) specifications. Because vegetable oils and derivatives thereof, such as **1–4** (Table 3), generally exhibit excellent lubrication characteristics, **1–4** were evaluated in fungible, nonadditized ULSD as potential lubricity enhancers. As indicated by Table 5, all materials imparted significantly enhanced lubricity to ULSD. In particular, esters **3** and **4** yielded wear scar data (HFRR, 60 °C) at ≥ 1 wt % in ULSD (<200 μ m) comparable to neat SME (162) and PME (172 μ m). Estolides **1** and **2** at similar concentrations provided wear scar lengths between 200 and 280 μ m, which is a substantial improvement over neat ULSD (551 μ m, Table 3). In fact, neat ULSD fails to meet the lubricity requirement specified in ASTM D975 (Table 1). Although pure estolides **1** and **2** exhibit superior lubricity in comparison to pure esters **3** and **4** (Table 3), when blended (wt %) with ULSD (Table 5) this trend is reversed, which is attributable to the considerably higher molecular weights (MW) of estolides **1** and **2** in comparison to esters **3** and **4**. In effect, although similar weight percentages of materials were used, the effective concentrations of estolides **1** and **2** were less than esters **3** and **4** in ULSD due to differences in the MW of the estolides as compared to the esters. Consequently, on a molecular level, fewer molecules of **1** and **2** are available to positively influence lubricity of ULSD when compared to **3** and **4** at similar weight percentages.

As with SME and PME, the low temperature performance and kinematic viscosity (40 °C) of **1–4** in ULSD were measured. Although neat **1–4** displayed considerably lower CP and PP values than ULSD, at additive levels in ULSD (>2 wt %), these materials failed to positively impact the low temperature performance of ULSD, as evidenced by the essentially unchanged CP and PP values shown in Table 5. As expected, with an increasing percentage of **1–4** in ULSD, a small increase in kinematic viscosity was observed (Table 5). However, all samples remained within ASTM D975 kinematic viscosity specifications (Table 1).

3.3. Effect of SME and PME on ULSD and Comparison with 1–4. Low level blends of BD with ULSD (B2–B20, i.e., 2% BD in ULSD in the case of B2) are variously and sporadically legislated in numerous regions around the world, including the United States and Europe. The beneficial effect of BD on the lubricity of ULSD is widely reported. As indicated by Table 5, SME imparts superior lubricity to ULSD at all blend ratios in comparison to PME. This result is explained by the higher saturated fatty ester content and generally shorter chain lengths of PME in comparison to SME (Table 2), both of which are known to have adverse effects on lubricity.²⁰ In comparison to **1–4**, PME is the least effective lubricity enhancer and esters **3** and **4** are the most effective. SME ranks between the esters (**3** and **4**) and estolides (**1** and **2**). Esters **3** and **4** were the only materials that imparted wear scars by HFRR < 200 μ m at 1 wt %.

As previously mentioned, BD is plagued with poor low temperature performance, which is attributable to the high melting points of saturated fatty esters contained within BD. Consequently, PME is more susceptible to solidification at subambient temperatures than SME. One strategy to improve the low temperature performance of BD is to blend with ULSD.

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At low blend levels (B0.1–B2.0) both SME and PME had no impact on the CP and PP of ULSD, which is essentially in agreement with results obtained for **1–4** in ULSD (Table 5). However, at higher blend ratios (B5 and especially B20), SME and PME had a negative effect on the CP and PP of ULSD. PME, which as mentioned previously has a higher saturated fatty ester content than SME, exhibited the most egregious low temperature behavior, especially at B20, providing CP and PP values of -8 and -12 °C, respectively (neat ULSD: CP -12 °C; PP -21 °C).

As expected, with an increasing percentage of SME and PME in ULSD, a small increase in kinematic viscosity was observed (Table 5). However, all samples remained within the ASTM D975 kinematic viscosity specification (Table 1). SME blends exhibited lower kinematic viscosities in comparison to PME blends at all blend levels, which is once again attributable to the higher saturated fatty ester content of PME. Previous studies confirm that saturated constituents have higher kinematic viscosities than their cis unsaturated counterparts.²¹ In comparison to **1–4**, SME blends had the least adverse effect on the kinematic viscosity of ULSD. All other materials (PME and **1–4**) displayed similarly detrimental behavior when blended with ULSD. However, all blends remained within the ASTM D975 kinematic viscosity specification.

4. Conclusions

The following conclusions are elucidated from the results discussed above:

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1. **1–4** imparted significantly improved lubricity to ULSD at low ($\leq 2\%$) blend levels. **3** and **4** are superior to both SME and PME, and **1** and **2** are superior to PME as lubricity enhancers at the same weight percent concentrations.

2. The CP values of SME and PME were unaffected by **1–4** at low blend levels ($\leq 5\%$). However, the PP of PME was improved by 3 °C at 5 wt % **1–4**. The PP of SME was essentially unchanged. These results indicate that **1–4** may be useful as PP depressants for PME in moderate temperature climates, but not for SME.

3. **1–4** were ineffective as either CP or PP depressants in ULSD. However, **1–4** did not adversely affect the CP or PP of ULSD.

4. Because **1–4** provided significantly improved lubricity to ULSD while not adversely affecting CP or PP, they may prove useful as substitutes for BD as lubricity enhancers in ULSD.

5. Although neat **1–4** exhibited high kinematic viscosities, at low blend levels in SME, PME, and ULSD, the kinematic viscosity remained within applicable specifications. As the blend level of **1–4** was increased in SME, PME, and ULSD, a small increase in kinematic viscosity was observed.

6. Biobased materials, such as **1–4**, show promise for fuel additive applications.

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