

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa



ORIGINAL ARTICLE



Thermo-oxidation, friction-reducing and physicochemical properties of ricinoleic acid based-diester biolubricants

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Received 24 June 2013; accepted 7 August 2013 Available online 20 August 2013

KEYWORDS

Oxirane ring opening; Low-temperature properties; Friction-reducing properties; TFMO test; Ricinoleic acid-based diesters

Abstract A major global effort is currently underway to reduce dependence on petroleum products and minimize the impact of their derivatives on the environment. Plant oils are being investigated as a potential source of environmentally favorable lubricants given their combination of biodegradability, renewability and excellent lubrication performance. Low oxidation and thermal stability, poor low-temperature properties and a narrow range of available viscosities, however, limit their potential application as industrial biolubricants. The chemical modification of plant fatty acid structures has great potential for improving the physicochemical and friction-reducing properties of these compounds. This paper presents the thermo-oxidation, friction-reducing and physicochemical properties of a series of diester compounds derived from ricinoleic acid as biolubricant basestocks. The results indicated that among the synthesized ricinoleic acid-based diester compounds, octyl 10,12-dihydroxy-9-behenoxystearate 16 has the lowest pour point $(-53.26 \,^{\circ}\text{C})$, while octyl 10,12-dihydroxy-9-octyloxystearate 10 has the highest onset temperature (128.98 °C) and the lowest volatile loss and quantity of insoluble deposits (68.78% and 77.25%, respectively). The frictionreducing results indicate an improvement occurred in the presence of longer mid-chain esters and an increased polarity in the ester functional group. The data indicate that some synthesized derivatives have significant potential as environmentally friendly biolubricant basestocks.

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Peer review under responsibility of King Saud University.



1. Introduction

Lubricants, as with any other oil, can affect the environment and the health of people who handle them throughout production, use and until disposal. During the last 25 years, the concerns for the environment and the use of biodegradable products have grown worldwide. In recent years, pollution and environmental health have become increasingly important

http://dx.doi.org/10.1016/j.arabjc.2013.08.002

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public matters (Erhan et al., 2008). In the case of lubrication, concerns have focused on the large quantity of lubricants that enter the environment and can break down into products that potentially threaten the environment. Water and soil are affected directly by loss lubrication systems while the air is affected by volatile lubricants or lubricant haze. The increased environmental awareness is the primary driving force for new technological developments, and special attention is being paid to environmental protection against pollution caused by lubricants based on mineral oils (Nagendramma and Kaul, 2008).

One of the greatest challenges is the development of universal biodegradable basestocks that could replace mineral oil basestocks in a new generation of biolubricants. From a performance standpoint, these substances should be environmentally friendly and eventually biodegradable (Pavlov et al., 2004). In general, plant oils have excellent properties for their potential use as biolubricants, such as a high-viscosity index, high lubricity, low volatility due to a high molecular weight and low toxicity combined with high biodegradability (Erhan and Asadaukas, 2000; Adhvarvu and Erhan, 2002). Thus, biolubricants are environmentally preferred to petroleumbased lubricants because they are more biodegradable and less toxic. However, plant oils normally have poor oxidative stability, which is largely due to the presence of bis-allylic protons. These active sites are highly susceptible to attack by oxygenated radicals, causing the subsequent oxidative degradation of the molecules that eventually results in polar oxy compounds and leads to insoluble deposits and increased oil acidity and viscosity (Asadauskas et al., 1996; Legarand and Dürr, 1998; Erhan et al., 2006).

Plant oils are primarily triacylglycerols, which are glycerol molecules with three saturated/unsaturated fatty acid chains attached via ester linkages at the hydroxyl groups. An excess of saturated long-chain fatty acids leads to poor low-temperature behavior, while an excess of certain poly-unsaturated fatty acids leads to unfavorable oxidation behavior. The unsaturated carbon-carbon bonds function as active sites for many reactions including oxidation (Adhvaryu et al., 2000). Even long monounsaturated fatty acids degrade the low-temperature behavior. The triacylglycerol structure gives these esters a high natural viscosity (and viscosity index) and is responsible for their structural stability over reasonable operating temperatures. Plant oils exhibit poor oxidation stability compared with mineral oils, and in general, they cannot withstand reservoir temperatures over 80 °C. These oils are also hydrolytically less stable, more likely to foam and have lower filterability than comparable mineral oils (Willing, 2001).

The deliberate modification of the chemical structures of plant unsaturated fatty acids has demonstrated a great potential for improving some of their excellent properties for use as biolubricant basestocks (Salih et al., 2011; Salimon et al., 2011a,b,c). In our previous work, several diester compounds were synthesized from commercially available ricinoleic acid and common fatty acids. The key step in the three-step synthesis included epoxidation and oxirane ring opening to yield the mono-ester derivatives. These derivatives were esterified with different alcohols in the presence of 10 mol% sulfuric acid to yield the desired diester compounds (Salimon et al., 2012a). As a continuation of the previous work, this work aims to study the effect of this modification on the physicochemical and friction-reducing properties of these compounds.

2. Materials and methods

2.1. Materials

Ricinoleic acid (95%) was obtained from Nu-Chek Prep, Inc. (Elysian, MN, USA). Formic acid (88%) and hydrogen peroxide (30% solution) were obtained from Fisher Scientific (Pittsburgh, PA). All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI). All materials were used without further purification. All organic extracts were dried using anhydrous magnesium sulfate (Aldrich Chemical).

2.2. Methods

2.2.1. Characterization

The ¹H and ¹³C NMR spectra were recorded using a JEOL JNM-ECP 400 spectrometer operating at frequencies of 400.13 and 100.77 MHz, respectively, with a 5-mm broadband inverse Z-gradient probe in DMSO-d₆ (Cambridge Isotope Laboratories, Andover, MA) solvent. Each spectrum was Fourier-transformed, phase-corrected and integrated using MestRe-C 2.3a (Magnetic Resonance Companion, Santiago de Compostela, Spain) software. The FTIR spectra were recorded directly on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45 ZeSe trough over a scanning range of 650–4000 cm⁻¹ using 32 scans to yield a spectral resolution of 4 cm⁻¹.

2.2.2. Pour point and cloud point

The pour points (PP) and cloud points (CP) were measured using the ASTM D5949 (ASTM, 2011a) and ASTM D5773 (ASTM, 2011b) methods, respectively, with a Phase Technology Analyzer, Model PSA-70S (Hammersmith Gate, Richmond, BC, Canada). The pour point, or the temperature at which a lubricant ceases to flow, is important in appraising the flow properties at low temperatures and, as such, can become the determining factor for selecting a lubricant. In addition, the pour point can be defined as the minimum temperature of a liquid, particularly a lubricant, below which the liquid ceases to flow and along with pump ability, the ease with which oil pumps at low temperatures, is a significant factor in cold-weather start-up. The cloud point is the lowest temperature at which the sample becomes clouded by the formation of wax crystals. Clouding is the only characteristic of paraffinic oils and is a consideration in the evaluation of fuels whose filtration might be impaired by the plugging effect of wax crystals. All runs were carried out at least twice, and the average values were reported with their standard deviations $(\pm SD).$

2.2.3. Viscosity index measurements

Automated multi-range viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure the viscosity. The measurements were made in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at 40.0 or 100.0 °C. The viscosity and the viscosity index were calculated using ASTM methods D445–97 (ASTM, 2011c) and D2270–93 (ASTM, 2011d), respectively. All measurements were made in triplicate, and the average values were reported with their standard deviations (±SD).

2.2.4. Pressure differential scanning calorimetry (PDSC) method

Oxidation is the predominate reaction experienced by a lubricant in service and accounts for many lubricant problems. Oxidation is the major cause of increased viscosity, varnish formation, sludge and sediment formation, additive depletion, base oil break-down, filter plugging, loss of foaming, rust and corrosion (Fox and Stachowiak, 2007). Therefore, understanding and controlling oxidation is a major concern for lubricant chemists. In this work, the oxidative stability experiments were performed using a DSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Typically, a 1.5–2.0 mg sample was placed in a hermetically sealed-aluminum pan with a pinhole lid for an interaction between the sample and the reactant gas (dry air). A film thickness of less than 1 mm was required to ensure proper oil-air interaction and eliminate any gas-diffusion issues. The dry air (Gateway Airgas, St Louis, MO) was pressurized in the module at a constant pressure of 1379 kPa. A 10 °C/min heating rate was used to raise the temperature of the materials from 50 to 350 °C during each experiment. The onset temperature (OT, °C) and the signal maximum temperature (SMT, °C) of the oxidation were calculated from the exothermal reaction of each sample. Each test was run in triplicate, and the average values were reported with their standard deviations (\pm SD).

2.2.5. The thin-film micro-oxidation (TFMO) method

The test oil (25 µL) was spread as a thin film on a freshly polished high-carbon steel catalyst surface and was oxidized by passing a steady flow (20 cm³/min) of dry air over the heated sample. The oxidation was carried out at a constant temperature (175 °C) inside a glass-bottomed reactor. The temperature was maintained at ± 1 °C by the placement of a heated aluminum slab atop a hot plate. This arrangement eliminated the temperature gradient across the aluminum surface and transferred the heat to the catalysts placed on the slab. The constant air flow ensured the removal of volatile oxidation products. The test was designed to eliminate any gas-diffusion limitations. After a specific time, the catalyst and the oxidized oil sample were removed from the oxidation chamber, rapidly cooled under a steady flow of dry N2 and immediately transferred to desiccators for temperature equilibration. After approximately 1 h, the catalyst containing the oxidized oil was weighed to determine the loss of volatile compounds due to thermal evaporation or the gain of material due to oxidation. The sample was then soaked in tetrahydrofuran (THF) for 30 min to dissolve the soluble portion of the oxidized oil. After dissolving the soluble oil. the catalyst containing the insoluble portion was placed into a desiccator to remove the last traces of the solvent. The sample was then weighed to determine the mass of the insoluble deposit. Each test was run in triplicate, and the average values were reported with their standard deviations $(\pm SD).$

2.2.6. The density determination method

The densities were determined at 20 °C based on the ASTM method D1298–99 (ASTM, 2011e) using a glass hydrometer provided by Lanxi Comp., Shanghai, China.

2.2.7. The volatility determination method

The volatility was determined in agreement with ASTM method D6184 (ASTM, 2011f) in an electrical stove using glass pans of 4 cm in diameter.

2.2.8. The friction-reducing test method

The friction-reducing determinations were performed according to ASTM method D4172–94 (ASTM, 2011g) using the four-ball method (Anton Paar Physica MCR301, Germany) with Rheoplus/32 V3.40 software. Each test was run in triplicate, and the average values were reported with their standard deviations (\pm SD).

2.3. Synthesis

2.3.1. Epoxidized ricinoleic acid (ERA) (2)

A hydrogen peroxide solution (30% in H₂O, 8.0 mL) was slowly added under stirring to a solution of ricinoleic acid (RA) **1** (95%, 15 g) dissolved in formic acid (88%, 14 mL) at 4 °C (ice bath). The reaction proceeded at room temperature with vigorous stirring (900 rpm) until a powdery solid formed in the reaction vessel (2–5 h). The solid was collected via vacuum filtration, washed with H₂O (chilled, 3×10 mL) and dried for 12 h under high vacuum to yield epoxidized ricinoleic acid (ERA) as a white, powdery solid (14.7 g, 93%).

2.3.2. 10,12-Dihydroxy-9-acyloxystearic acid (DHASA) (3-9)

The fatty acids (6 g) were added slowly over 1.5 h to a mixture of epoxidized ricinoleic acid 2 (31 g) and *p*-toluenesulfonic acid (PTSA) (5 g) in toluene, and the temperature of the reaction mixture was maintained below 70–80 °C. The reaction mixture was subsequently heated to 90–100 °C and refluxed for 3 h. After the reaction was completed, the solution was cooled to room temperature and stirred overnight. The next day, the mixture was washed with water, the organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using a vacuum evaporator.

2.3.3. Octyl 10,12-dihydroxy-9-acyloxystearate (ODHAS) (10–16)

The reaction scheme for the formation of the diesters is provided in Fig. 1. Sulfuric acid (conc. H_2SO_4 , 10 mol-%) was added to a stirred suspension of 10,12-dihydroxy-9-acyloxy-stearic acid **3–9** (3.35 mmol) in octanol (3.35 mL). The suspension was stirred and heated at 60 °C for 10 h. Then, hexane (5 mL) was added and the solution was washed once with saturated aqueous NaHCO₃ (0.5 mL) and brine (2 × 1 mL), dried (MgSO₄), filtered, and concentrated under vacuum for 6 h to yield octyl 10,12-dihydroxy-9-acyloxystea-rate derivatives.

3. Results and discussion

3.1. Synthesis

Generally, epoxidized plant oils provide promising intermediates for the utilization of plant oils as biolubricant basestocks



Octyl 10,12-dihydroxy-9-acyloxystearate (ODHAS, 10-16)

Figure 1 The reaction scheme for the formation of diesters.

because the epoxide, or oxirane, group can easily be functionalized and chemically modified. In this work, the first step, as shown in Fig. 1, was the epoxidation of ricinoleic acid 1 using formic acid and hydrogen peroxide to yield epoxidized ricinoleic acid 2. The second step was the opening of the oxirane ring in the epoxidized oil by attacking it with octanoic, nonanoic, lauric, myristic, palmitic, stearic and behenic acids to yield the respective 9(10)-hydroxy-10(9)-ester derivatives of ricinoleic acid 3–9. The diester-derivatives of 10,12-dihydroxy-9-acyloxystearate 10–16 were prepared by the esterification of the seven corresponding acyloxy-derivatives using octanol and sulfuric acid.

3.2. Characterization

All synthesized compounds were characterized via 1 H, 13 C NMR and FTIR spectroscopy. Significant signals found in the 1 H spectrum of the epoxidized ricinoleic acid **2** at ~2.2

and 2.4 ppm correspond to protons on the quaternary carbons of the oxirane ring, whereas a double in the ¹³C spectrum at \sim 56.82 and 56.86 ppm corresponds to the carbons of the oxirane ring. Furthermore, the ¹H spectrum of the epoxidized ricinoleic acid 2 exhibited singlet signals at ~ 9.15 and \sim 9.32 ppm, which represent the protons of the -OH groups (Campanella et al., 2010). In contrast, a singlet at ~9.12-9.29 ppm represents the -OH protons, and the bands at \sim 2.03–3.64 ppm correspond to $-CH_2$ - groups in the ¹H spectra of the 10,12-dihydroxy-9-acyloxystearic acid 3-9 derivatives. The ¹H spectra of octyl 10,12-dihydroxy-9acyloxystearate 10-16 consist of multiplet signals at ~9.18-9.35 ppm due to – the –OH protons and at \sim 1.42–3.24 ppm due the -CH₂-, -CH(OH) and -CH(OCOR) protons, respectively. Furthermore, the signals at $\sim 173.1 - 176.7$ ppm in the ¹³C NMR spectra are attributed to the ester carbonyl groups (Salimon et al., 2012a). These signals are in agreement with the proposed structures.

The structures of the ester functional groups were also confirmed via IR spectral analysis. Bands representing the ester C=O group (~1740 cm⁻¹), the CH₃ group (~1376 cm⁻¹), the OH group (~3478–3443 cm⁻¹) and the C–O–C functionality (~1000–1100 cm⁻¹) are clearly visible in the spectra (Sliverstein et al., 2005).

3.3. Low-temperature properties and the viscosity index

In this work, seven fatty acids were chosen for investigating the effects of various alkyl groups on the low-temperature properties of the synthesized products (Table 1). These fatty acids were chosen based on the length of their carbon-chain backbone, which was medium (C_8-C_{12}) to long $(C_{14}-C_{22})$. The presence of long saturated fatty acids in the compounds does not allow easy stacking of the individual molecules due to disruptions in the molecular symmetry. As a result, microcrystalline structures form instead of macro structures. At low temperatures, such microcrystalline structures can easily tumble and glide over one another enhancing the fluidity of the liquid, i.e., the attachment of an ester side chain of optimum length at the 9 or 10 position of the fatty acid chain can significantly improve its lowtemperature properties (Hawang and Erhan, 2001). While epoxidized ricinoleic acid 2 has a pour point of 9.16 °C and a cloud point of 12.31 °C; the synthesized esters 3-16 all have significantly improved pour points ranging from -10.22 to -53.26 °C, and cloud points in the range -7.58--49.75 °C.

In practice, a biolubricant should be useful over a broad temperature range; in cold weather, the range of lubricant low-temperature performance is measured through the pour point (PP) and the cloud point (CP), which represent the primary drawbacks of plant oil biolubricants (Salimon et al., 2011b). Plant oils are complex molecular substances in which the transition from liquid to solid does not occur at a unique temperature, but over a relatively wide range and involves several polymorphic crystalline shapes (α , β' , β) that depend on the unsaturated/saturated fatty acid ratio (Sato, 2001; Adhvaryu et al., 2003; Govindapillai et al., 2009). The pour point (PP) and cloud point (CP) of a biolubricant are good indicators of its low-temperature fluidity (Salimon et al., 2012b).

The viscosity is the most important physical property of a lubricant. The viscosity, which may be defined as a liquid's resistance to flow, is the characteristic most frequently stipu-

Table 1 The physicochemical properties of the samples.					
Samples	Density (g/cm ³)	Volatility at 120 °C (%)	Pour point/ $^{\circ}C^{a}$	Cloud point/ $^{\circ}C^{a}$	Viscosity index (VI) ^a
2 , ERA	0.734	1.77	9.1 ± 0.34	12.31 ± 0.67	67.10 ± 1.66
3, DHOSA	0.765	1.63	-10.22 ± 0.54	-7.58 ± 0.53	110.70 ± 3.24
4, DHNSA	0.787	1.51	-13.29 ± 0.27	-11.19 ± 0.49	117.89 ± 3.67
5, DHLSA	0.792	1.40	-15.38 ± 0.44	-13.52 ± 0.28	125.57 ± 4.11
6, DHMSA	0.813	1.33	-17.10 ± 0.73	-15.73 ± 0.36	146.69 ± 4.82
7, DHPSA	0.845	1.20	-18.32 ± 0.29	-16.14 ± 0.51	155.61 ± 5.03
8, DHSSA	0.867	1.12	-20.44 ± 0.60	-18.89 ± 0.72	163.90 ± 5.45
9, DHBSA	0.884	1.06	-23.19 ± 0.41	-20.65 ± 0.39	171.53 ± 6.17
10, ODHOS	0.891	0.93	-26.35 ± 0.27	-23.20 ± 0.28	195.41 ± 7.20
11, ODHNS	0.912	0.85	-28.27 ± 0.38	-26.34 ± 0.42	237.76 ± 10.34
12, ODHLS	0.924	0.72	-33.40 ± 0.56	-31.80 ± 0.31	242.80 ± 10.89
13, ODHMS	0.937	0.67	-39.38 ± 0.71	-34.54 ± 0.63	257.59 ± 11.20
14, ODHPS	0.945	0.60	-44.22 ± 0.43	-41.22 ± 0.25	266.78 ± 11.65
15, ODHSS	0.960	0.53	-48.19 ± 0.29	-45.78 ± 0.64	276.34 ± 12.17
16, ODHBS	0.978	0.48	-53.26 ± 0.57	-49.75 ± 0.58	282.29 ± 12.49

ERA, epoxidized ricinoleic acid; DHOSA, 10,12-dihydroxy-9-octyloxystearic acid; DHNSA, 10,12-dihydroxy-9-nonanoxystearic acid; DHLSA, 10,12-dihydroxy-9-lauroxystearic acid; DHMSA, 10,12-dihydroxy-9-myristoxystearic acid, DHPSA; 10,12-dihydroxy-9-palmitoxystearic acid; DHSSA, 10,12-dihydroxy-9-stearoxystearic acid; DHSSA, 10,12-dihydroxy-9-behenoxystearic acid; ODHOS, octyl 10,12-dihydroxy-9-octyl-oxystearate; ODHNS, octyl 10,12-dihydroxy-9-nonanoxystearate; ODHLS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHSS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHSS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHSS, octyl 10,12-dihydroxy-9-stearoxystearate; ODH

^a Mean \pm SD.

lated by equipment manufacturers when making lubricant recommendations. The viscosity index, commonly designated VI, is an arbitrary numbering scale that indicates the variation of oil's viscosity with changes in temperature. A low viscosity index indicates that the viscosity changes greatly with temperature. Therefore, a fluid that has a high viscosity index is expected to undergo little change in viscosity with temperature extremes and is considered to have a stable viscosity. A fluid with a low viscosity index is expected to undergo significant changes in viscosity as the temperature fluctuates. Furthermore, the viscosity of a lubricant is closely related to its ability to reduce friction (Sharma et al., 2009; Salimon et al., 2011a).

The results (Table 1) indicate that an overall increase in the molecular weights of the products resulting from the increased chain length of the ester functionality in longer mid-chain groups increases the viscosity index.

3.4. Thermo-oxidative stability

Epoxidized ricinoleic acid 2, 10,12-dihydroxy-9-acyloxystearic acid 3–9, and octyl 10,12-dihydroxy-9-acyloxystearate 10-16 were screened for their oxidation stability using pressurized differential scanning calorimetry to determine the onset temperature (OT) and the signal maximum temperature (SMT). The oxidation onset temperature is a relative measure of the degree of oxidative stability in a material evaluated for a given heating rate and oxidation environment. For example, in oxygen, a higher OT value indicates a more oxidatively stable material. The signal maximum temperature is the temperature at which maximum heat output is observed in the sample during oxidative degradation. A higher SMT value does not necessarily correlate with improved oxidative stability.

The ability of a material to resist oxidation is represented by its oxidative stability, which plays a major role in its aging, shelf-time and other performance characteristics. To avoid these problems, biolubricants must possess superior oxidative stability. The results in Table 2 indicate that a general improvement in the oxidative stability was observed in the synthesized compounds **3–16** as the chain length of the mid-chain ester decreased because longer side chains have additional accessible sites that can easily oxidized making them more susceptible to cleavage than short chains (Salih et al., 2011).

Pressure differential scanning calorimetry (PDSC) has several advantages: First, an oxidative stability test may make too long at atmospheric pressures to be convenient. Second, some reactions from water or methanol as a byproduct, leading to foaming in the sample, can be suppressed at higher pressures. Third, some reaction kinetics is affected by the pressure; therefore, running the reaction under controlled pressure is necessary for kinetics studies. Finally, pressure differential scanning calorimetry is an effective way to rapidly measure the oxidative tendencies of biolubricant base oils, plant oils and oleochemicals (Fox and Stachowiak, 2007).

Oxidative degradation has been identified as the most important limiting factor for lubricant application. The consequences of lubricant oxidation include increased acidity and viscosity, varnish formation, sludge and sediment formation, additive depletion, base-oil breakdown, filter plugging, rust and corrosion (Luna et al., 2011). Therefore, understanding and controlling oxidation is a major concern for improving biolubricant basestock properties (Wagner, 2001; Schneider, 2006; Sharma et al., 2007).

Another thermal-oxidative stability test was performed using thin-film micro-oxidation (TFMO) to study the volatility and the depository tendencies of the synthesized ester products. In most applications, a biolubricant functions as a thin film, so the thin-film micro-oxidation test is considered a good choice to simulate actual conditions under which oxygen diffusion is unlimited (Adhvaryu et al., 2006). Micro-oxidation is a family of thin-film oxidation tests that is widely used by the lubricant industry (Perez et al., 1987), and its results are consistent with those of pressure differential scanning calorimetry (Dunn, 2005). During the oxidation process, some small primary oxidation products are lost as volatile compounds, while

Samples	Onset temperature (OT)/°C ^a	Signal maximum temperature (SMT)/°C ^a
2, ERA	60.23 ± 2.45	228.98 ± 10.23
3, DHOSA	105.41 ± 3.18	214.64 ± 9.60
4, DHNSA	98.78 ± 2.69	232.21 ± 10.36
5, DHLSA	95.7 ± 2.51	239.44 ± 10.48
6, DHMSA	90.19 ± 2.34	200.72 ± 9.12
7, DHPSA	82.25 ± 2.02	256.69 ± 11.10
8, DHSSA	75.60 ± 1.89	223.43 ± 9.85
9, DHBSA	64.82 ± 1.72	240.10 ± 10.52
10, ODHOS	128.98 ± 3.48	87.39 ± 2.18
11, ODHNS	119.11 ± 2.93	176.28 ± 5.80
12, ODHLS	97.08 ± 2.35	255.26 ± 11.97
13, ODHMS	92.43 ± 2.20	139.48 ± 4.56
14, ODHPS	84.92 ± 1.89	188.57 ± 7.12
15, ODHSS	78.68 ± 1.75	153.31 ± 4.76
16, ODHBS	67.46 ± 1.34	110.38 ± 3.79

Table 2 The PDSC data of the samples showing the onset of oxidation and the signal maximum temperatures

15, ODHSS78. 68 ± 1.75 153.31 ± 4.76 16, ODHBS 67.46 ± 1.34 110.38 ± 3.79 ERA, epoxidized ricinoleic acid; DHOSA, 10,12-dihydroxy-9-octyloxystearic acid; DHNSA, 10,12-dihydroxy-9-nonanoxystearic acid; DHLSA, 10,12-dihydroxy-9-lauroxystearic acid; DHMSA, 10,12-dihydroxy-9-myristoxystearic acid; DHPSA, 10,12-dihydroxy-9-palmitoxystearic acid; DHSSA, 10,12-dihydroxy-9-stearoxystearic acid; DHBSA, 10,12-dihydroxy-9-behenoxystearic acid; ODHOS, octyl 10,12-dihydroxy-9-octyl-oxystearate; ODHNS, octyl 10,12-dihydroxy-9-nonanoxystearate; ODHLS, octyl 10,12-dihydroxy-9-stearoxystearate;dihydroxy-9-myristoxystearate; ODHPS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHSS, octyl 10,12-dihydroxy-9-stearoxystearate;

ODHBS, octyl 10,12-dihydroxy-9-behenoxystearate.

^a Mean \pm SD.

others undergo oxy-polymerization to form oil-insoluble deposits in the presence of excess oxygen. The ability to form such deposits is the primary restriction to the use of unsaturated oleochemicals as high-temperature biolubricants. The

Table 3	The	thin-film	micro-oxidation	test	data	of	the
samples a	t 175	°C.					

1		
Samples	Volatile loss (%) ^a	Insoluble deposit (%) ²
2 , ERA	65.87 ± 1.75	73.78 ± 2.43
3, DHOSA	72.43 ± 2.19	81.67 ± 2.65
4, DHNSA	80.51 ± 2.80	89.43 ± 2.91
5, DHLSA	88.74 ± 3.12	94.52 ± 3.11
6, DHMSA	96.82 ± 3.46	102.34 ± 3.29
7, DHPSA	108.48 ± 3.87	112.80 ± 3.97
8, DHSSA	114.52 ± 4.10	123.61 ± 4.13
9, DHBSA	128.31 ± 4.54	140.75 ± 4.80
10, ODHOS	68.78 ± 2.02	77.25 ± 2.23
11, ODHNS	71.05 ± 2.10	81.11 ± 2.46
12, ODHLS	85.46 ± 2.74	90.48 ± 3.04
13, ODHMS	93.34 ± 3.15	95.39 ± 3.57
14, ODHPS	99.16 ± 3.67	103.64 ± 4.13
15, ODHSS	105.75 ± 4.29	117.53 ± 4.46
16, ODHBS	120.52 ± 4.67	128.79 ± 5.51

ERA, epoxidized ricinoleic acid; DHOSA, 10,12-dihydroxy-9octyloxystearic acid; DHNSA, 10,12-dihydroxy-9-nonanoxystearic acid; DHLSA, 10,12-dihydroxy-9-lauroxystearic acid; DHMSA, 10,12-dihydroxy-9-myristoxystearic acid; DHPSA, 10,12-dihydroxy-9-palmitoxystearic acid; DHSSA, 10,12-dihydroxy-9-stearoxystearic acid; DHBSA, 10,12-dihydroxy-9-behenoxystearic acid; ODHOS, octyl 10,12-dihydroxy-9-octyloxystearate; ODHNS, octyl 10,12-dihydroxy-9-nonanoxystearate; ODHLS, octyl 10,12-dihydroxy-9myristoxystearate; ODHMS, octyl 10,12-dihydroxy-9myristoxystearate; ODHPS, octyl 10,12-dihydroxy-9myristoxystearate; ODHPS, octyl 10,12-dihydroxy-9notystearate; ODHS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHSS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHS, octyl 10,12-dihydroxy-9-behenoxystearate; ODHBS, octyl 10,12-dihydroxy-9-stearoxystearate; ODHBS, octyl 10,12-dihydroxy-9-stearoxystearate; ODHBS, octyl 10,12-dihydroxy-9-behenoxystearate; ODHBS,

^a Mean \pm SD.

volatile loss obtained from thin-film micro-oxidation tests can be used to predict the useful life of a biolubricant.

In this work, a thin-film micro-oxidation test was carried out on all synthesized products 2-16; the data from these samples are presented in Table 3. One can observe that the losses due to high-temperature volatility and insoluble deposits increased gradually as the number of carbon atoms bound to epoxy carbons in the mid-chain ester group increased (i.e., when the length of mid-chain substituents increased) due to an increased likelihood of oxidative degradation (Dunn, 2005). These results are in agreement with those obtained via pressure differential scanning calorimetry (Table 2).

3.5. Friction-reducing measurements

Table 4 shows the friction-reducing results for the synthesized compounds 2–16. The results indicate that an improvement in the friction-reducing properties (reduced wear scar diameter (WSD)) values and coefficient of frictions (μ)) occurred with longer mid-chain esters and an increased polarity in the ester functional group substituents, i.e., diester > monoesters (Table 4), due to the increased polar functional groups in the product structures, which increased the strength of the friction-reducing film at the metal contact zone and thereby increased its efficiency in reducing the friction (Biresaw et al., 2003; Kurth et al., 2005; Sharma et al., 2009). Beside this; increasing in branching points of mid-chain group which increase the polarity separation between the long non polar chain with ester functionality group resulting in increase the tendency of ester functional group attach onto metal surfaces (Salih et al., 2013).

The surface of the machinery components can appear well finished to the naked eye. When magnified, however, surface imperfections become readily apparent. These microscopic hills and valleys are called asperities (Brophy and Zisman,

Table 4 The friction-reducing properties of the synthesized compounds in the four-ball test.				
Samples	Four ball wear scar diameter (WSD),40 daN, 1 h (mm) ^a	Coefficient of friction (μ)		
2, ERA	1.14 ± 0.13	0.75		
3, DHOSA	0.98 ± 0.10	0.71		
4, DHNSA	0.92 ± 0.12	0.68		
5, DHLSA	0.88 ± 0.11	0.65		
6, DHMSA	0.85 ± 0.13	0.61		
7, DHPSA	0.81 ± 0.10	0.57		
8, DHSSA	0.76 ± 0.12	0.53		
9, DHBSA	0.70 ± 0.10	0.46		
10, ODHOS	0.63 ± 0.13	0.39		
11, ODHNS	0.58 ± 0.11	0.33		
12, ODHLS	0.52 ± 0.12	0.29		
13, ODHMS	0.47 ± 0.13	0.25		
14, ODHPS	0.42 ± 0.10	0.20		
15, ODHSS	0.38 ± 0.11	0.17		
16, ODHBS	0.33 ± 0.10	0.14		

ERA, epoxidized ricinoleic acid; DHOSA, 10,12-dihydroxy-9-octyloxystearic acid; DHNSA, 10,12-dihydroxy-9-nonanoxystearic acid; DHLSA, 10,12-dihydroxy-9-lauroxystearic acid; DHMSA, 10,12-dihydroxy-9-myristoxystearic acid; DHPSA, 10,12-dihydroxy-9-palmitoxystearic acid; DHSSA, 10,12-dihydroxy-9-stearoxystearic acid; DHSSA, 10,12-dihydroxy-9-behenoxystearic acid; ODHOS, octyl 10,12-dihydroxy-9-octyl-oxystearate; ODHNS, octyl 10,12-dihydroxy-9-nonanoxystearate; ODHLS, octyl 10,12-dihydroxy-9-stearoxystearate; ODHS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHS, octyl 10,12-dihydroxy-9-stearoxystearate; ODHS, octyl 10,12-dihydroxy-9-palmitoxystearate; ODHS, octyl 10,12-dihydroxy-9-stearoxystearate; ODHS, octyl 10,12-dihydroxy-9-stearoxystearat

^a Mean \pm SD.

1951). When dry surfaces move relative to one another, asperities may rub, lock together, and break apart. The resistance generated when these adjacent surfaces come into contact is called friction (Rabinowicz, 1995; Biresaw et al., 2002, 2003). Another consequence of friction is that the energy created by resistance is converted into heat. A lubricant is any material that is interposed between surfaces, forming a film to avoid or minimize contact between the surfaces (Salimon and Salih, 2009a). An important property of biolubricants is their ability to maintain a stable lubricating film at the metal contact zone. Plant oils and fatty esters are known to provide excellent lubricity due to their ester functionality. The ester ends of the fatty acid chain adsorb onto the metal surfaces, thus forming a monolayer film with the hydrocarbon end of the fatty acids oriented away from the metal surface (Salimon and Salih, 2009b,c; Salimon et al., 2011c, 2012b).

4. Conclusions

Lubrication is a complicated process, and a single lubricating oil cannot necessarily work under all conditions. To qualify for broad industrial use, a biolubricant must have low-temperature stability and excellent lubricating properties. These properties are inherent weakness in bio-based lubricants.

Based on the obtained results, as the chain length of the mid-chain ester (the acyloxy group) increased, a corresponding improvement was observed in the low-temperature behavior due to the increased ability of the longer chain esters to destroy the crystalline formation at lower temperatures. In addition, an increase in the chain length of the mid-chain ester had a positive influence on the friction-reducing characteristics of the synthesized derivatives due to the increasing the polar functionality in the structure, which leads to stronger adsorption onto the metal surface and enhanced lateral interactions between the ester chains. However, the trends in the pour points run counter to those in the thermo-oxidative stability as demonstrated by the pressure differential scanning calorimetry and thin-film micro-oxidation data: increasing the length of the mid-chain ester has a negative influence on thermo-oxidative stability. In general, the ricinoleic acid-based diester derivatives exhibit better physicochemical and friction-reducing properties than their precursors rendering them good candidates for biolubricant basestocks.

Acknowledgments

The authors thank the Universiti Kebangsaan Malaysia for funding ("Code AP-2011-17", "DPP-2013-054" and "UKM-MI-OUP-2011").

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