Synthesis, Characterization and Physicochemical Properties of Oleic Acid Ether Derivatives as Biolubricant Basestocks

Jumat Salimon¹*, Nadia Salih† and Emad Yousif²

¹ School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia (43600 Bangi, Selangor, MALAYSIA)
² Department of Chemistry, College of Science, Al-Nahrain University (Baghdad, IRAQ)

Abstract: Petroleum is a finite source as well as causing several environmental problems. Therefore petroleum needs to be replaced by alternative and sustainable sources. Plant oils and oleochemicals derived from them represent such alternative sources; the use of oleochemicals as biobased lubricants is of significant interest. This article presents a series of chemical modification on oleic acid to yield synthetic biolubricant basestocks. Measuring of density, volatility, cloud point (CP), pour point (PP), flash point (FP), viscosity index (VI), onset temperature (OT) and signal maximum temperature (SMT) was carried out for each compound. Furthermore, the friction and wear properties were measured using high-frequency reciprocating rig (HFRR). The results showed that octadecyl 9-octadecyloxy-10-hydroxyoctadecanoate exhibited the most favorable low-temperature performance (CP -26°C, PP -28°C) and the lowest ball wear scan diameter (42 μm) while propyl 9-propyloxy-10-hydroxyoctadecanoate exhibited the higher oxidation stability (OT 156°C).

Key words: plant oil, biolubricant, chemical modification, pour point, onset temperature.

1 INTRODUCTION

There are several positive reasons for the use of plant oils, or plant oil derivatives as lubricants. Because as much as 40% of a lubricant can be lost to the environment, the inherent biodegradability of plant oils serves to reduce their environment impact. Plant oils as lubricants are preferred because they are biodegradable and non-toxic, unlike conventional mineral-based oils. They have very low volatility due to the high molecular weight of the triacylglycerol molecule and have a narrow range of viscosity changes with temperature. Polar ester groups are able to adhere to metal surfaces, and therefore, possess good boundary lubrication properties. In addition, plant oils have high solubilizing power for polar contaminants and additive molecules.

However, the disadvantage for the usage of plant oils in lubricants is its poor thermooxidative stability. Plant oil oxidizes like hydrocarbon mineral oil following the same free radical oxidation mechanism but at a faster rate. The faster oxidation of plant oils is due to the presence of unsaturated fatty acids present in it. Bis-allylic hydrogens in linoleic and linolenic fatty acids are susceptible to free radical attacks, peroxide formation and production of polar oxidation products.

One potential way to solve the problems which restricted the use of plant oil as biolubricants is through chemical derivatization of olefinic groups of the oleochemical. Hydrogenation, transesterification, epoxidation and alkylation, or a combination of chemistries have all been used in order to synthesis an improved products.

Herein we describes the synthesis of a series of α-hydroxy ethers from 9,10-epoxystearates (Fig. 1) utilizing both head group manipulation and branching strategies to impart favorable low-temperature, oxidative stability and lubricity properties of these lipid-based materials. Other physicochemical parameters for these products were also measured. The results may help in the development of biobased lubricant.

* † Correspondence to: Jumat Salimon; Nadia Salih, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA
E-mail: jumat@ukm.my; nadiaas@ukm.my
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2 EXPERIMENTAL PROCEDURES

2.1 Chemicals

Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA, USA) and oleic acid (99%) from Nu-Chek Prep, Inc. (Elyria, MN). 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 Structural analysis

$^1$H and $^{13}$C NMR spectra were recorded using a JEOL JNM-ECP 400 spectrometer operating at a frequency of 400.13 and 100.77 MHz, respectively, using a 5-mm broadband inverse Z-gradient probe in DMSO-$_d_6$ (Cambridge Isotope Laboratories, Andover, MA) as solvent. Each spectrum was Fourier-transformed, phase-corrected, and integrated using MestRe-C 2.3a (Magnetic Resonance Companion, Santiago de Compostela, Spain) software. FTIR spectra were recorded neat on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45°ZSe trough in a scanning range of 650-4,000 cm$^{-1}$ for 32 scans at a spectral resolution of 4 cm$^{-1}$.

2.3 Determination of lubricant properties

Cloud point (CP) and pour point (PP) determinations were made in agreement with ASTM D6594$^{15}$ using a Phase Technology Analyzer, Model PSA-70 S (Hammersmith Gate, Richmond, B.C., Canada). Each sample was run in triplicate and average values rounded to the nearest whole degree are reported. CP and PP data are rounded to the nearest whole degree. The pour point is defined as the temperature (°C) where the sample continues to pour from a tilted jar. Statistically the method has shown quite good consistency for determining low temperature flow properties of fluids.

Flash point (FP) determination was run according to the American National Standard Method using a Tag Closed Tester (ASTM D 56-79)$^{16}$. Each sample was run in triplicate and the average values rounded to the nearest whole degree are reported. The flash point is the lowest temperature, to which a biolubricant must be heated before its vapor, when mixed with air, will ignite but not continue to burn. The flash point is the temperature at which biolubricant combustion will be sustained.

Automated multi range viscometer tubes HV M472 obtained from Walter Herzog (Germany) were used to measure viscosity. Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL, USA) viscometer bath set at 40.0 and 100.0°C. The viscosity and viscosity index were calculated using ASTM methods D 445-97$^{17}$ and ASTM D 2270-93$^{18}$, respectively. Triplicate measurements were made and the average values were reported.

Oxidative stability experiments were accomplished by using pressurized differential scanning calorimetry (PDSC), DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE). Typically, a 2-µL sample that resulted in a film thickness of less than 1 mm was placed in an aluminum pan hermetically sealed with a pinhole lid. This was oxidized in the presence of dry air (Gateway Airgas, St Louis, MO), which was pressurized in the module at a constant pressure of 1,378.95 kPa (200 psi). Each experiment utilized a 10°C per min heating rate to get from 50 to 350°C. The oxidation onset (OT, °C) and signal maximum temperatures (SMT, °C) of oxidation were calculated from the exotherm in each case. Each sample was run in triplicate and average values rounded to the nearest whole degree are reported.

Lubricity determinations were performed at 60°C, according to ASTM method D 6079$^{19}$ using a high-frequency reciprocating rig (HFRR) lubricity tester (PCS Instruments, London, UK) via Laser Scientific (Granger, IN, USA). The average wear scar diameter of each replicates was determined by calculating the average of the x- and y-axis wear scar length. Each experiment was conducted in triplicate and the data is reported as mean ± SD of triplicate determinations.

2.4 Synthesis of epoxidized oleic acid (EOA), 2 and alkyl 9-alkyloxy-10-hydroxyoctadecanoate (AAHOD), 3-11

Hydrogen peroxide solution (30% in H$_2$O, 8.0 mL) was
added slowly into a stirred solution of oleic acid (OA) \(1\) (99%, 15 g) in formic acid (88%, 14 mL) at 4°C (ice bath). The reaction proceeded at room temperature with vigorous stirring (900 rpm) until the formation of a powdery solid was noticed in the reaction vessel (2-5) h. The solid was collected via vacuum filtration, washed with \(\mathrm{H}_2\mathrm{O}\) (chilled, 3 × 10 mL), and placed for 12 h under high vacuum to provide epoxidized oleic acid (EOA) as a colorless, powdery solid.

To a stirred suspension of epoxidized oleic acid \(2\) (1.0 g, 3.35 mmol) in the appropriate alcohol (3.35 mmol) was added \(\mathrm{H}_2\mathrm{SO}_4\) (conc., 10 mol%). The alcohols used were propyl, isopropyl, butyl, pentyl, hexyl, 2-ethylhexyl, decyl, hexadecyl and octadecyl alcohols. The suspension was heated with stirring at 60°C for (20-22) h. After reaction termination, the solution was washed with \(\mathrm{NaHCO}_3\) (sat. aq., 1 × 0.5 mL) and brine (2×1 mL), dried (\(\mathrm{MgSO}_4\)), filtered, concentrated in vacuo and placed for 12 h under vacuum to yield the desired products.

### 3 RESULTS AND DISCUSSION

#### 3.1 Synthesis and characterization

The first step in the synthesis is an epoxidation reaction of oleic acid, as shown in Fig. 1, using formic acid and hydroxide peroxide to give epoxidized oleic acid (EOA). Many nucleophilic reagents are known to add to an oxirane ring, resulting in ring opening. In this work, ring opening reaction of EOA was done using propanol, isopropanol, butanol, pentanol, hexanol, 2-ethylhexanol, decanol, hexadecanol and octadecanol to give respective 9(10)-hydroxy-10(9)-ether ester derivatives. The straightforward epoxidation of oleic acid was closely monitored to avoid the synthesis of the undesired 9,10-dihydroxyoctadecanoate, which will failure the system due to loss of kinetic energy of individual molecules during self-stacking. All synthetic products described above were screened for low-temperature behavior through determination of their cloud point (CP) and pour point (PP)

An improvement in the cold flow behavior of AAHOD was obtained over that of their precursor epoxidized oleic acid (EOA) (Table 1). The presence of long saturated fatty acids in the compounds does not allow individual molecules easily stack due to disruption in the symmetry of the molecules. As a result, microcrystalline structures form instead of macro-structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another enhancing the fluidity of the liquid.

The viscosity of a biolubricant is its tendency to resist flow. A biolubricant oil of high viscosity flows very slowly. The viscosity must always be high enough to keep good oil film between the moving parts. Otherwise, friction will increase, resulting in power loss and rapid wear on the parts.

The viscosity index, commonly designated VI, is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. Each type of oil has a viscosity index based on the slop of the temperature-viscosity curve. A high index means a flatter slope, or lesser variation of viscosity with the same changes in temperature. If biolubricant oil with a high viscosity index is used, its viscosity will change less when the temperature of the engine increases. Knowing the viscosity index of oil is crucial when selecting a biolubricant for an application, and is especially critical in extremely hot or cold climates. Failure to use oil with the proper viscosity index when temperature extremes are expected may result in poor lubrication and equipment failure.

In general, from the viscosity index data of synthesized compounds (Table 1) it can be seen that viscosity index increases with chain length (number of carbons). A high viscosity index indicates small oil viscosity changes with tem-

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**Table 1**

<table>
<thead>
<tr>
<th>Chain length</th>
<th>Viscosity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12</td>
<td>26</td>
</tr>
<tr>
<td>C14</td>
<td>23</td>
</tr>
<tr>
<td>C16</td>
<td>22</td>
</tr>
<tr>
<td>C18</td>
<td>24</td>
</tr>
</tbody>
</table>

---
The flash point can be used to determine the transporta-
sion and storage temperature requirements. Biolubricant
The flash point can be used to determine the transporta-

tus design, the condition of the apparatus used, and the
behave as a potential biolubricant is to evaluate the oils
products, such as lubricants, surfactants, and fuels. There-
Another important fact in determining how well oil will
The ability of a substance to resist oxidative degradation
 Another important attribute for a number of industrial
The flash point can be used to determine the transporta-
and special precautions for safe handling. In this investiga-
which maximum heat output is noted from the sample
during oxidative degradation. A higher SMT does not nec-
arily correlate with improved oxidative stability. In the
present study, as the chain length of the mid and end-chain
ester is decreased, a corresponding improvement in oxida-
tion stability was observed, which is because longer chains
are more susceptible to oxidative cleavage than shorter
chains. The data also shows that AAHOD compounds have
higher OT than their precursor, EOA. This is in agreement
with the general rule; decreasing unsaturation number in
oil samples increases the oxidation stability.

One of the most important properties of biolubricants is
their ability to maintain a stable lubricating film at the
metal contact zone. Fatty acid esters are known to provide
excellent lubricity due to their ester functionality. The
polar heads of the fatty acid esters attach to metal surfaces
and allow a monolayer film formation with the non-polar
end of fatty acids sticking away from the metal surface.
Fatty acid esters are known to provide
stable lubricating film at the
metal contact zone. Fatty acid esters are known to provide
excellent lubricity due to their ester functionality. The
polar heads of the fatty acid esters attach to metal surfaces
and allow a monolayer film formation with the non-polar
end of fatty acids sticking away from the metal surface.
The fatty acid alkyl chains offer a sliding surface that pre-
vents the metal-to-metal direct contact. When a film is not
form, metal-to-metal contact may result in rising tempera-
ture at the contact zones of moving parts causing adhesion,
scuffing or even welding. The epoxy group offers active
oxygen sites that trigger binding on the metal surface
forming a protective film. This protective film builds further
with time to reduce friction.

In this work, the antiwear and friction reducing proper-
ties of synthetic ester oil basestocks were evaluated using
high-frequency reciprocating rig (HFRR) lubricity tester. The
HFRR method determines the lubricity or ability of a
fluid to affect friction and wear between the surfaces in
relative motion under load. The average ball scar diameter,

Table 1  Density, volatility, cloud point (CP), pour point (PP), flash point (FP), viscosity index (VI), onset temperature (OT) and signal maximum temperature (SMT) of synthesized products.

<table>
<thead>
<tr>
<th>R group, Compound No.</th>
<th>Density [g/cm³]</th>
<th>Volatility, 120°C [%]</th>
<th>CPb [°C]</th>
<th>PPb [°C]</th>
<th>FPb [°C]</th>
<th>VId</th>
<th>OTb [°C]</th>
<th>SMTb [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOA, 2</td>
<td>0.804</td>
<td>1.05</td>
<td>10</td>
<td>0</td>
<td>113</td>
<td>45</td>
<td>75</td>
<td>164</td>
</tr>
<tr>
<td>Pr, 3</td>
<td>0.908</td>
<td>1.30</td>
<td>-8</td>
<td>-11</td>
<td>124</td>
<td>95</td>
<td>156</td>
<td>201</td>
</tr>
<tr>
<td>iPr, 4</td>
<td>0.915</td>
<td>1.22</td>
<td>-10</td>
<td>-13</td>
<td>113</td>
<td>113</td>
<td>144</td>
<td>212</td>
</tr>
<tr>
<td>Bu, 5</td>
<td>0.926</td>
<td>1.16</td>
<td>-14</td>
<td>-18</td>
<td>189</td>
<td>120</td>
<td>135</td>
<td>199</td>
</tr>
<tr>
<td>Pe, 6</td>
<td>0.933</td>
<td>1.09</td>
<td>-17</td>
<td>-20</td>
<td>170</td>
<td>126</td>
<td>127</td>
<td>215</td>
</tr>
<tr>
<td>Hx, 7</td>
<td>0.937</td>
<td>0.93</td>
<td>-19</td>
<td>-22</td>
<td>177</td>
<td>131</td>
<td>116</td>
<td>226</td>
</tr>
<tr>
<td>2-EH, 8</td>
<td>0.947</td>
<td>0.86</td>
<td>-21</td>
<td>-24</td>
<td>159</td>
<td>143</td>
<td>105</td>
<td>205</td>
</tr>
<tr>
<td>De, 9</td>
<td>0.954</td>
<td>0.77</td>
<td>-23</td>
<td>-25</td>
<td>216</td>
<td>166</td>
<td>94</td>
<td>247</td>
</tr>
<tr>
<td>HD, 10</td>
<td>0.962</td>
<td>0.65</td>
<td>-24</td>
<td>-26</td>
<td>178</td>
<td>191</td>
<td>83</td>
<td>222</td>
</tr>
<tr>
<td>OD, 11</td>
<td>0.987</td>
<td>0.54</td>
<td>-26</td>
<td>-28</td>
<td>233</td>
<td>215</td>
<td>77</td>
<td>227</td>
</tr>
</tbody>
</table>

a EOA = epoxidized oleic acid; Pr = propyl; iPr = isopropyl; Bu = butyl; Pe = pentyl; Hx = hexyl; 2-EH = 2
ethylhexyl; De = decyl; HD = hexadecyl; OD = octadecyl.
b ± 1 °C
Table 2  HFRR lubricity data of synthesized products.

<table>
<thead>
<tr>
<th>R group, Compound No.</th>
<th>Ball wear scar diameter (μm)</th>
<th>Disc wear scar width on X-axis (μm)</th>
<th>Disc wear length on X-axis (μm)</th>
<th>Film (%)</th>
<th>CoF</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOA, 2</td>
<td>145 ± 2</td>
<td>148 ± 3</td>
<td>255 ± 40</td>
<td>67</td>
<td>1.210</td>
</tr>
<tr>
<td>Pr, 3</td>
<td>122 ± 2</td>
<td>130 ± 3</td>
<td>210 ± 43</td>
<td>71</td>
<td>0.096</td>
</tr>
<tr>
<td>iPr, 4</td>
<td>113 ± 2</td>
<td>126 ± 2</td>
<td>198 ± 35</td>
<td>75</td>
<td>0.089</td>
</tr>
<tr>
<td>Bu, 5</td>
<td>105 ± 3</td>
<td>109 ± 2</td>
<td>185 ± 41</td>
<td>86</td>
<td>0.085</td>
</tr>
<tr>
<td>Pe, 6</td>
<td>90 ± 2</td>
<td>103 ± 2</td>
<td>166 ± 48</td>
<td>90</td>
<td>0.078</td>
</tr>
<tr>
<td>Hx, 7</td>
<td>82 ± 3</td>
<td>95 ± 2</td>
<td>156 ± 44</td>
<td>93</td>
<td>0.066</td>
</tr>
<tr>
<td>2-EH, 8</td>
<td>73 ± 3</td>
<td>89 ± 2</td>
<td>149 ± 39</td>
<td>95</td>
<td>0.056</td>
</tr>
<tr>
<td>De, 9</td>
<td>66 ± 3</td>
<td>78 ± 3</td>
<td>134 ± 41</td>
<td>97</td>
<td>0.050</td>
</tr>
<tr>
<td>HD, 10</td>
<td>58 ± 3</td>
<td>71 ± 2</td>
<td>191 ± 46</td>
<td>97</td>
<td>0.045</td>
</tr>
<tr>
<td>OD, 11</td>
<td>42 ± 2</td>
<td>63 ± 2</td>
<td>178 ± 49</td>
<td>98</td>
<td>0.040</td>
</tr>
</tbody>
</table>

Values are mean ± SD of triplicate determinations

width of wear track on disk at x-axis, film percentage, and coefficient of friction (CoF) for synthetic oils are shown in Table 2. The higher values for antiwear and friction reducing properties are obtained from AAHOD compounds. A possible explanation for our results is that the extra oxygen moieties on these compounds help the compounds adhere to the metal surface and reduce friction especially under load. These molecules undergo chemical transformation at the metal contact zone and develop a stable tribocatalytic film for further protection.

Unfortunately the used lubricants are usually deposited in the environment and endangering our planet. To solve the problem, lubricants should be manufactured from plant oil derivatives. There are several industrial application possibilities for fatty acid esters, as natural compounds. Oleic acid (cis-9-octadecenoic acid) is one of the most important fatty acids in nature; it can be produced from plant oils. Its esters can be applied as biolubricant basestocks. These finding promote us to synthesis alkyl 9-alkoxy-10-hydroxyoctadecanoate (AAHOD) through ring opening reaction of epoxidized oleic acid. In general, all the products produced in this study showed reasonable and acceptable physicochemical properties to be applied for biolubricant use. These products are plausible to replace petroleum-based lubricant which is non biodegradable and possess environmental harm. Thus the synthesized oleic acid-based ether products are useful and can be good candidate for general purpose biolubricant use such as chain saw machine, break fluid, transmission oil and etc.

4 CONCLUSION

This study presents the effect of chemical structure modification on the physicochemical properties of plant oils. Based on the results obtained, increase the chain length of the mid- and end-chain alkyl group had a positive influence on the low temperature and anti-wear properties of ring opening products because they create a steric barrier around the individual molecules and inhibits crystallization, resulting in lower cloud and pour points. The trend for CP and PP run counter to that of OT; i.e., increasing chain length is a beneficial to CP and PP, but a detrimental to OT. From these results, a future study will aim to strike a balance between the opposing properties through investigation of a greater variety of mid-chain ester groups. Furthermore, in general the ester ether compounds AAHOD have improved antiwear and friction properties than their precursors.

ACKNOWLEDGEMENTS

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*J. Oleo Sci.* 60, (12) 613-618 (2011)
16) *ASTM Standard D 56-79*: Standard test method for flash point of liquids with a viscosity less than, 45 Saybolt Universal Seconds (SUS) at 37.8°C (that don’t contain suspended solids and don’t tend to form a surface film under test).
18) *ASTM D 2270-93*: Standard practice for calculating viscosity index from kinematic viscosity at 40 and 100°C. ASTM, West Conshohocken, PA (USA).