Australian Journal of Basic and Applied Sciences, 4(7): 1999-2003, 2010
ISSN 1991-8178

Chemical Modification of Oleic Acid Oil for Biolubricant Industrial Applications

[1]Jumat Salimon and [2]Nadia Salih

[1]School of Chemical Sciences & 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: There has been a lot of interest in using vegetable oils as renewable raw materials for new industrial products including lubricants. This emphasis on environmentally friendly lubricants is largely due to the rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution from excessive mineral oil use. Vegetable oils are promising candidates as base fluid for ecofriendly lubricants, but their use is restricted due to low thermo-oxidative stability and poor cold flow behavior. This paper presents use chemically modified triesters derived from oleic acid to improve the oxidation and cold flow behavior. Here, we report the oxirane ring opening of epoxidized oleic acid using behenic acid and *p*-toluenesulfonic acid (PTSA) as catalyst followed by esterification reaction with octanol and 2-ethylhexanol to form diesters (compounds 3 and 4), respectively. The remaining free hydroxyl group was reacted with oleic and stearic acid to give triesters (compounds 5 and 6), respectively. One of the products, compound 6, was shown to have pour point, flash point and viscosity indices of -60 °C, 305 °C, and 193 cp, respectively, which are favourable properties in biolubricant applications. The structures of the products were confirmed by FTIR, ^{1}H- and ^{13}C-NMR.

Key words: chemically modified vegetable oil, pour points, oxidation stability, biolubricants.

INTRODUCTION

There has been a constant demand for environmentally friendly lubricants. A significant lubricant market of some 9 million metric tons per year of industrial and automotive lubricants exists. There is an increasing concern for environmental pollution from excessive petroleum based lubricants use and their disposal especially in lost lubrication, military applications, and in outdoor activities such as forestry, mining, railroads, dredging, fishing and agriculture hydraulic systems. Over 60 % of the lubricants used in the U.S. are lost to the environment (Gawrilow, 2004). Vegetable oils with high oleic content are considered to be potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters (Hwang *et al.*, 2001). Vegetable oils are preferred over synthetic fluids because they are renewable resources and cheaper (Adhvaryu *et al.*, 2005). Furthermore, vegetable oils lubricants are biodegradable and non-toxic, unlike conventional mineral-based oils (Thames *et al.*, 1999). 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, vegetable oils have high solubilizing power for polar contaminants and additive molecules (Dinda *et al.*, 2008).

On the other hand, vegetable oils have poor oxidative stability primarily due to the presence of bis allylic protons and are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds. This phenomena result in insoluble deposits and increases in oil acidity and viscosity (Jayadasa *et al.*, 2007). Vegetable oils also show poor corrosion protection. The presence of ester functionality renders these oils susceptible to hydrolytic breakdown (Wua *et al.*, 2000).

Therefore, contamination with water in the form of emulsion must be prevented at every stage. Low temperature study has also shown that most vegetable oils undergo cloudiness, precipitation, poor flow, and solidification at -10 ˚C upon long-term exposure to cold temperature (Schuster *et al.*, 2008) in sharp contrast to mineral oil-based fluids. These physical and chemical properties can be improved either using genetically modified oils or chemically modified oil with suitable combination of additives (Moser *et al.*, 2008). Oleic

---

Corresponding Author: Jumat Salimon, School of Chemical Sciences & Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.
E-mail: jumat@ukm.my
Tel: +60 3 8921 5412; Fax: +60 3 8921 5410

acids are more thermally stable than polyunsaturated fats, and therefore are highly desired component in vegetable oils for lubricant applications. Breeding successes helped to develop high oleic vegetable oils, which are now available for commercial uses. On the other hand, modification of the oil through chemical processing to improve oxidation stability and low temperature fluidity is also possible. These two options in combination with chemical additive offer the greatest opportunity for achieving the ultimate goal. This study presents use of chemical modification to improve the cold flow behavior of vegetable oils for the use as biolubricant base oil.

MATERIALS AND METHODS

Materials:

Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA, USA) and oleic acid (99%) from Nu-Chek Prep, Inc. (Elysian, MN, USA). All other chemicals and reagents were obtained from Aldrich Chemical (Milwau-kee, WI, USA). All materials were used without further purification. All organic extracts were dried using anhydrous magnesium sulfate.

Syntheis of Epoxidized Oleic Acid (1):

Hydrogen peroxide solution (30% in H2O, 8 mL) was added slowly into a stirred solution of oleic acid (90%, 10 g) in formic acid (88%, 9 mL) at 4 C (ice bath). Then the reaction proceed at room temperature with vigorous stirring (900 rpm) until the formation of a white, powdery solid was noticed in the reaction vessel for 2-5 hours. The solid was colllected via vacuum filtration, washed with H2O (chilled, 3 × 10 mL), and placed for 12 hours under vacuum to provide epoxidized oleic acid as a colorless, powdery solid.

Synthesis of 9(10)-hydroxy-10(9)-behnyloxystearic Acid (2):

Epoxidized oleic acid (1, 31 g) and 5g of p-toluenesulfonic acid (PTSA) was dissolved in toluene in 250 mL three-neck flask equipped with a cooler, dropping funnel and thermometer. The mixture was kept at 50 C. Behenic acid (6 g) was added during 1.5 hours in order to keep the reaction mixture temperature under 70-80 C. The reaction mixture was subsequently heated to 90-100 C and refluxed for 3 hours at this temperature range. After reaction termination, the heating was stopped and the mixture was left to stand overnight at ambient room tempearture. The mixture was then washed with water, the organic layer was dried over anhydrous magnesium sulfate and the solvent was removed using vacuum evaporator to give the desired product.

Synthesis of Alkyl 9(10)-hydroxy-10(9)- Behnyloxystearate (3 and 4):

Sulfuric acid (conc. H_2SO_4, 10 mol-%) was added to a solution of 9(10)-hydroxy-10(9)-acyloxystearic acid (2, 1 g) in either 3.35 mL octanol or 3.35 mL 2-ethylhexanol.. The suspension was heated with stirring at 60 °C for 10 hours. Hexanes (5 mL) was then added, and the solution was washed with $NaHCO_3$ (sat. aq., 1 × 0.5 mL) and brine (2 × 1 mL), dried ($MgSO_4$), filtered, concentrated in *vacuo* and placed under vaccum for 6 hours. to yield the desired compounds of (3) or (4), respectively.

Synthesis of Modified Triesters (5 and 6):

To a solution of alkyl 9(10)-hydroxy-10(9)-behnyloxystrearate (3 or 4, 10 g) and sulfuric acid (10% H2SO4) in a two-neck round bottom flask equipped with a magnetic stir bar at room temperature; then thereaction mixture was refluxed with stirring for 10 hours. After the reaction was transferred to a separatory funnel, the lower aqueous phase wasremoved, and hexane (20 mL) was added to the upper oily phase. The organic phase wasthen washed with NaHCO3 (sat. aq., 2 × 5 mL) and brine (2 × 5 mL), died (MgSO4), filtered, concentrated in vacuo and placed under high vacuum for 6 hours to provide the triesters (5 and 6).

Instrumentation:

Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer GX FTIR Spectrophotometer (USA). The ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-ECP 400 spectrometer (400MHz ^{1}H/ 100.61MHz ^{13}C) using DMSO-d_6 as a solvent in all experiment. All the physical properties analyses were performed in duplicate according to the standard methods (AOCS official method) for flash point and pour point. Viscosity measurements were made using calibrated Brookfield Viscometer. The spindle size 4 was used with the speed of 100 rpm. Viscosity reading is in centipoise (cp) and the unit is in mPa°s (*multipascal second*).

RESULTS AND DISCUSSION

Synthesis:

In this work, we start our reaction sequence, Fig. 1, with epoxidation of oleic acid (Salimon and Salih, 2009 a) to yield epoxidized oleic acid (1). Then, we open the oxirane ring using behenic acid and *p*-toluenesulfonic acid (PTSA) as catalyst (Salimon and Salih, 2009 b). This step of the reaction gave 9(10)-hydroxy-10(9)-behnyloxystearic acid (2) not 9(10)-hydroxy-10(9)-benyloxystearic acid formation from 9,10-epoxyoleic acid with a yield 65%. Esterification of the oleic acid carbonyl was done using octanol and 2-ethylhexanol in order to prepare alkyl 9(10)-hydroxy-10(9)-behnyloxystearate (3 and 4) with a yield 73% and 65%, respectively.

The two prepared diesters of 9,10-hydroxy-acyloxystearic acid were used as a key for the synthesis of modified trimesters-derivatives by esterification of the hydroxy diester groups with either oleic acid and stearic acid. The yields are summarized in Table 4.

Infra-Red Spectroscopy:

The structures of the synthesized compounds were confirmed using Fourier-Transformed Infrared (FTIR) spectroscopy. The characteristic signals in the FTIR spectrum of epoxidized oleic acid (1) at 830, 845cm^{-1} correspond to quaternary carbons of the oxirane ring (Erhan, *et al.*, 2006) and the signals at 2987 and 2865 cm^{-1} correspond to aliphatic carbons in the molecules. In mono-ester product (2) the bands at 1738 and 1710 cm-1 due to C=O stretching vibrations of ester and carboxylic acid moieties confirm the success of oxirane ring opening step. Furthermore, the most characteristic evidence confirms triester formation was the disappearance of OH stretching vibration around 3400 cm^{-1}. Other characteristic FTIR data are summarized in Table 1.

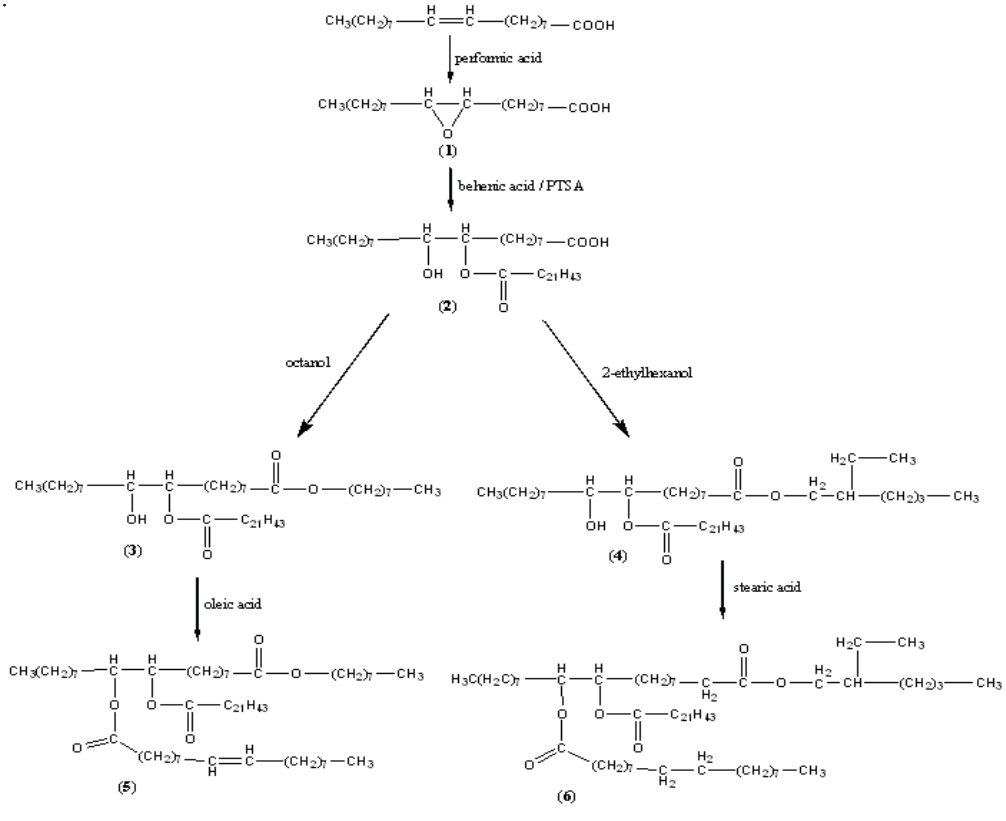


Fig. 1: Synthetic pathway for compounds 1-6.

Table 1: Characteristic FTIR absorption data of compounds (1-6)

compound	υ (O-H)	υ (C-H) aliphatic	υ (C=O)	υ(-C-O-C)
1	3425	2987, 2865	1708	830, 845
2	3441	2946, 2872	1738, 1710	-
3	3453	2947, 2822	1730	-
4	3412	2943, 2826	1727	-
5	-	2937, 2891	1733	-
6	-	2982, 2865	1734	-

NMR Spectroscopy:

All prepared compounds displayed good solubility in DMSO. The nuclear magnetic resonance spectral data gave additional support for the composition of the compounds. The observed changes are evidences of the reaction had happened because the chemical shift of a compound is heavily depended on its electronic environment. The ^{1}H-NMR spectra of the triester compounds (5 and 6) confirmed the disappearance of OH signal at about 9.40-9.65 ppm. Furthermore, at about δ 2.15-3.57 ppm resonance the protons signals of the aliphatic $-CH_2-$ chain were appeared for the prepared compounds (Sliverstien *et al.*, 2005). Other characteristic data are tabulated in Table 2.

The ^{13}C-NMR data of the prepared products are presented in Table 3. The C=O resonance group of the products appear at about 170.36-174.62 ppm. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to it (Sliverstien *et al.*, 2005). In the case of compounds (2-4) there are two signals while in with compounds (5 and 6) there are three signals in this range. These results were in agreement with the proposed structures which given to these compounds.

Table 2: ^{1}H-NMR spectral (δ, ppm) data of prepared products

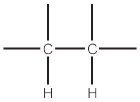
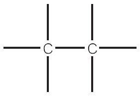
compound	$-CH_3$	CH_2 aliphatic	 $-\underset{H}{\overset{\vert}{C}}-\underset{H}{\overset{\vert}{C}}-$	CH=CH-	O-H
1	1.13-1.54	2.30-3.52	4.50-5.37	-	8.55
2	1.24-1.62	2.28-3.57	4.47-5.40	-	8.51, 9.25
3	1.53-1.76	2.15-3.52	4.53-5.40	-	8.52, 9.32
4	1.23-1.80	2.40-3.53	4.32-5.35	-	8.40, 9.34
5	1.21-1.53	2.37-3.56	4.42-5.44	5.29, 5.63	-
6	1.19-1.67	2.31-3.55	4.50-5.41	-	-

Table 3: ^{13}C-NMR spectral (δ, ppm) data of prepared products

compound	$-CH_3$	$-CH_2-$	 $-\underset{\vert}{\overset{\vert}{C}}-\underset{\vert}{\overset{\vert}{C}}-$	-CH=CH-	C=O
1	22.56-24.34	26.56-41.30	60.67, 62.53	-	172.67
2	21.32-24.78	26.45-40.65	60.62, 62.55	-	171.43, 174.62
3	22.67-24.87	26.43-40.51	60.60, 62.54	-	170.86, 173.56
4	20.85-24.11	26.50- 40.34	60.56, 62.50	-	170.86, 173.56
5	22.35-25.12	26.51-40.54	60.56, 62.47	62.42, 64.32	171.43, 173.14, 174.08
6	22.50-24.52	26.45-40.28	60.57 62.53	-	171.54, 172.48, 174.60

Effect of Chemical Modification on Physical Properties:

There is an important fact in determining how well an oil will behave as a potential lubricant is to evaluate the pour point (PP). The low temperature flow property of vegetable oils is extremely poor and this limits their use at low operating temperatures especially as automotive and industrial fluids. In the high-oleic oils removal of polyunsaturation (low unsaturation numbers) results in improved cold flow property due to reduction in saturated fatty acids. However, the high oleic oils are still limited in their use in low temperature applications (Erhan *et al.*, 2005).

The prepared compounds (2–6) described above were screened for low-temperature behavior through determination of both CP and PP. Modified triester exhibited a PP of -35 ˚C (Table 4), which is an improvement over that of other compounds. As expected, as the chain length of the ester increased, a corresponding improvement in PP is observed, which may be due to the greater ability of the longer-chain esters to more effectively disrupt macrocrystalline formation at reduced temperatures. A positive effect on the low-temperature performance of the resultant products was observed when a branched alcohol, 2-ethyl hexanol, was used. For instance, compound (6) has PP of -35 °C, whereas compound (5) has PP of -31 °C. This improvement in PP is observed, which may be due to the greater ability of the branch-chain esters to more effectively disrupt macrocrystalline formation at reduced temperatures.

Table 4: Pour point, flash point, viscosity values and percentage yield of prepared products.

compound	Pour point (°C)	Flash point (°C)	Viscosity (cp)	Yield (%)
1	-	140	-	70
2	-	232	-	65
3	-23	142	129	73
4	-28	165	149	65
5	-31	176	159	87
6	-35	300	178	92

Conclusions:

Within the current study, several basic trends were observed. The prepared compounds (2–6) exhibited the favorable cold-flow characteristics, as determined by PP. Compound (6) yielded the best performance with PP of –35 °C. The presence of branching group at the head of the molecule will make it more effectively in disruption crystalline formation at reduced temperatures. These products may prove useful in the search for bio-based industrial materials, such as biolubricants.

ACKNOWLEDGEMENT

The authors acknowledge the Universiti Kebangsaan Malaysia for funding ("Code UKM-GUP-NBT-08-27-113" and "UKM-OUP-NBT-29-150/2010"), and the direct contributions of the support staff from the School of Chemical Sciences and Food Technology, the Faculty of Science and Technology, Universiti Kebangsaan Malaysia.

REFERENCES

Adhvaryu, A., Z. Liu, and S.Z. Erhan, 2005. Synthesis of Novel Alkoxylated Triacylglycerols and Their Lubricant Base Oil Properties. Ind. Crops Prod., 21: 113-119.

Dinda, S., A.V. Patwardhan, V.V. Goud and N.C. Pradhan, 2008. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. Bioresource Technology, 99: 3737–3744.

Erhan, S.Z., B.K. Sharma and J.M. Perez, 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. Ind. Crops Prod., 24: 292–299.

Erhan, S.Z., B.K. Sharma and J.M. Perez, 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. Ind. Crops Prod., 24: 292–299.

Gawrilow, I., 2004. Vegetable Oil Usage in Lubricants. Inform, 15: 702-705.

Hwang, H., and S.Z. Erhan, 2001. Modification of Epoxidized Soybean Oil for lubricant Formulations with Improved Oxidative Stability and Low Pour Point. J. Am. Oil Chem. Soc., 78: 1179-1184.

Jayadasa, N.H., K.P. Nair and G. Ajithkumar, 2007. Tribological evaluation of coconut oil as an environment-friendly lubricant. Tribology International, 40: 350–354.

Moser, B.R., S.C. Cermak and T.A. Isbell, 2008. Valuation of Castor and Lesquerella Oil Derivatives as Additives in Biodiesel and Ultralow Sulfur Diesel Fuels. Energy & Fuels, 22: 1349–1352.

Salimon, J. and N. Salih, 2009 a. Improved Low Temperature Properties of 2-Ethylhexyl 9(10)-Hydroxy-10(9)-Acyloxystearate Derivatives. Eur. J. Sci. Res., 31(4): 583-591.

Salimon, J. and N. Salih, 2009 b. Oleic Acid Diesters: Synthesis, Characterization and Low Temperature Properties. Eur. J. Sci. Res., 32(2): 216-222.

Schuster, H., L.A. Rios, P.P. Weckes and W.F. Hoelderich, 2008. Heterogeneous catalysts for the production of new lubricants with unique properties. Appl. Cat. A: General, 348: 266–270.

Silverstien, R.M., G. Bassler and T. Morrill, 2005. Spectrometric Identification of Organic Compounds. 7th Edn., John-Wiley, New York.

Thames, S.F. and H. Yu, 1999. Cationic UV-Cured Coatings of Epoxide-Containig Vegetable Oils. Surf. Coat. Technol., 115: 2-3.

Wua, X., X. Zhanga, S. Yangb, H. Chena and D. Wanga, 2000. The Study of Epoxidized Rapeseed Oil Used as a Potential Biodegradable Lubricant. J. Am. Oil Chem. Soc., 77(5): 561-563.