Bio-lubricants Derived from Waste Cooking Oil with Improved Oxidation Stability and Low-temperature Properties

Weimin Li and Xiaobo Wang*

State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 73000, People’s Republic of China

Abstract: Waste cooking oil (WCO) was chemically modified via epoxidation using H₂O₂ followed by transesterification with methanol and branched alcohols (isooctanol, isodecanol and isooctadecanol) to produce bio-lubricants with improved oxidative stability and low temperature properties. Physicochemical properties of synthesized bio-lubricants such as pour point (PP), cloud point (CP), viscosity, viscosity index (VI), oxidative stability, and corrosion resistant property were determined according to standard methods. The synthesized bio-lubricants showed improved low temperature flow performances compared with WCO, which can be attributing to the introduction of branched chains in their molecular structures. What’s more, the oxidation stability of the WCO showed more than 10 folds improvement due to the elimination of −C=C− bonds in the WCO molecule. Tribological performances of these bio-lubricants were also investigated using four-ball friction and wear tester. Experimental results showed that derivatives of WCO exhibited favorable physicochemical properties and tribological performances which making them good candidates in formulating eco-friendly lubricants.

Key words: bio-lubricant, waste cooking oil, chemical modification, low-temperature properties, oxidative stability

1 Introduction

Increasing environmental awareness and growing regulations over pollution and contamination have accelerated the development of renewable and biodegradable lubricants. Vegetable oils that were the first lube oils and still served as a source of renewable raw materials. They are applied in modern lubricants either directly; in formulations containing vegetable oils such as soybean and rapeseed oils, or as precursors for the manufacture of chemically modified base oils and effective additives. The former approach has lower energy processing requirements but gives a very limited range of products, whose usefulness is limited by their relatively poor oxidative control, reduced operating temperature ranges, poor low temperature operability and their availability in limited viscosity ranges. Greater flexibility of utilization is achieved through chemical modification, such as epoxidation, estolide formation and transesterification. A remarkably large series of papers and reviews investigated the epoxidication of −C=C− bonds in the triglycerides to obtain interesting fluids for lubricating formulation.

Erhan and co-workers have worked on the chemical modification of soybean oil to produce bio-lubricants. Their reports show that epoxidized soybean oil can be used as high-temperature lubricant and a series of low temperature lubricant productions can be obtained from ring opening of the epoxide groups followed by the esterification of the resulting hydroxyl to attach a side branch alkyl group. Kurth et al. found the friction coefficient of epoxidized soybean oil in hexadecane and polyalphaolefin significantly reduced and its oxidative stability is also improved compared to their olefinic counterparts. It was also reported that the epoxidized plant oil could be served as lubricating additives and for metal working fluids. Moser et al. reported that the diesters of oleic acid produced by ring opening esterification of epoxidized oleic esters show improved oxidative stability and cold flow property. Gryglewicz and Akermana developed vegetable oil based trimethylolpropane (TMP) ester from vegetable oils methyl ester through transesterification. Transesterification eliminates the β-hydrogen atom of the vegetable oil substrate, thus improving the oxidative and thermal sta-
bility of the bio-lubricant base-stock.\(^\text{13,14}\) Honary et al. systematically investigated genetically modified high oleic soybean oil based lubricant and developed dozens of bio-lubricants.\(^\text{15-17}\)

Although oil crops are renewable resources, bio-lubricant from oil crops in large quantities has been deemed unsustainable.\(^\text{18}\) Production of bio-lubricant from oilseed crops will require large areas of arable land. This has lead to compete with the cultivation of oilseed crops and thus is currently a huge controversial issue.\(^\text{19}\) These problems highlight the need for alternative resources that could be more economic than traditional oilseed crops and wouldn’t raise controversy in food security.

Waste cooking oil (WCO), which is 2 to 3 times less than the cost of fresh vegetable oil, is a promising alternative to vegetable oils for bio-lubricant production.\(^\text{19}\) At present over 18 million tons of WCO are produced from restaurants, eating establishments and food industries around the world.\(^\text{20}\) WCO primarily consists of triglycerides, mostly unsaturated fatty acids with glycerol.\(^\text{21}\) It shares most of the salutary properties of other vegetable oils as lubricants except some physical and chemical changes as compared to the fresh vegetable oil after frying. Theoretically, WCO can be considered as a sustainable source for the production of low cost bio-lubricant. However, most researches related to waste cooking oils are focused on the use of fatty acids from WCO for the production of biodiesel.\(^\text{19,20}\) There is few literatures reported chemical modification of WCO to produce bio-lubricants.\(^\text{22,23}\)

In this paper, waste cooking oil is chemically modified to produce bio-lubricants. Three WCO-based fluids were synthesized and considered as base stocks for eco-friendly lubricants. Typical properties of these bio-lubricants such as viscosity, viscosity index, pour point, cloud point; corrosion resistant, oxidative stability and four-ball anti-wear (AW) properties were investigated.

2 Materials and Methods

2.1 Materials

Acetic acid (99.8 wt.%), hydrogen peroxide (30 wt.%), calcium oxide, and isooctanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, CHN). Isotridecanol and isooctadecanol were obtained from Far Eastern Group (Laiyang, CHN). Amberlyst 15 (30 g, 20 w% of WCO) were added, then the mixture was heated to 65°C followed by addition of 30% aqueous hydrogen peroxide (12.5g, 1.2 mol of hydrogen peroxide per mole of ethylenic unsaturation). The above mixture was allowed to react at 65°C for 10 h with continuous magnetic stirring at 1000 rpm. The reaction product was filtered and extracted with diethyl ether in separating funnel, purified with 5% NaHCO\(_3\) three times to neutralize free acid, and then analyzed for oxirane content 5.4\%, iodine value 8.8 g I\(_2\) /100 g of oil and glycol content of 0.08 mol of 100 g of oil. Yield, 142 g.

2.2 Analytical methods

Fourier transform infrared (FTIR) spectra were recorded on a Bruker-Optics TENSOR 27 FT-IR system (Rein-stetten, Germany) equipped with a KBr beam splitter. A regular scanning range of 400-4000 cm\(^{-1}\) was used for 16 repeated scans at a spectral resolution of 4 cm\(^{-1}\) in thin film condition using a pair of KBr crystals. All the spectra were recorded and processed using the OPUS data processing software.\(^\text{1}\) HNMR was recorded on a Bruker AVANCE III-600 spectrometer (Bruker, Switzerland) at frequencies of 600 MHz. For the \(^1\)H experiment, sample solutions were prepared in deuterated chloroform (CDCl\(_3\), 99.8\% D). The oxirane oxygen content of sample was determined using the method ASTM D1652.

2.3 Preparation of WCO derivatives and analysis

2.3.1 Synthesis of epoxidized waste cooking oil (EWCO)

The waste cooking oil (WCO) (150 g) was placed in a 500 mL three-necked flask, the required quantity of acetic acid (12.4 g, carboxylic acid to ethylenic unsaturation molar ratio, 0.25:1) and Amberlyst 15 (30 g, 20 w% of WCO) were added, then the mixture was heated to 65°C followed by addition of 30% aqueous hydrogen peroxide (12.5g, 1.2 mol of hydrogen peroxide per mole of ethylenic unsaturation). The above mixture was allowed to react at 65°C for 10 h with continuous magnetic stirring at 1000 rpm. The reaction product was filtered and extracted with diethyl ether in separating funnel, purified with 5% NaHCO\(_3\) three times to neutralize free acid, and then analyzed for oxirane content 5.4\%, iodine value 8.8 g I\(_2\) /100 g of oil and glycol content of 0.08 mol of 100 g of oil. Yield, 142 g.

2.3.2 Epoxidized fatty acid methyl ester preparation (EFAME)

120 g of epoxidized WCO (EWCO), 15 g of methanol, and 0.3 g of CaO were placed in a 250 mL round bottom flask, equipped with a magnetic stirrer and capped with a reflux condenser and placed in a water bath. The bath temperature was maintained at 70°C. The reaction was carried out for 2 h. Then the mixture was cooled down to ambient temperature and the resulting two layers were separated. The upper layer contained a solution of epoxidized fatty acid methyl ester (EFAME). Then the mixture was concentrated under vacuum and the product of EFAME was obtained which was used in the following step without purification. Yield, 108 g.

2.3.3 Transesterification

Epoxidized fatty acid esters of branched alcohols were synthesized by transesterification EFAME with isooctanol, isotridecanol and isooctadecanol, respectively. A hundred grams of EFAME, 46.8 g of isooctanol, 72.1 g of isotrideca-
Bio-lubricant base fluids based on renewable raw materials (waste cooking oil)

danol or 97.4 g of isoctadecanol, and 0.3 g of CaO used as catalyst were placed in a 250 mL three neck flask. The flask equipped with a thermometer, a sampling port and a reflux condenser. The condenser was connected to a vacuum line equipped with a relief valve, accumulator and a vacuum trap. The vacuum was gradually applied to the system until it reached the desired pressure and maintained at the same pressure. The methanol formed by the reaction was continuously removed. The quantity of the methanol was used to measure the conversion of the reaction. The reaction temperatures were 90°C, 120°C or 140°C for react with isoctanol, isostearecanol and isoctadecanol, respectively. When the reaction complete, the synthesized ester was separated from the catalyst by vacuum filtration and the excess branched alcohol was removed using a vacuum evaporator. Figure 1 shows the process for segmentation and functionalization of waste cooking oil (WCO) into epoxidized branched esters.

Fig. 1 Schematic of the process for segmentation and functionalization of waste cooking oil (WCO) into epoxidized branched esters.

The FTIR spectra of WCO and synthesized bio-lubricants (EWO, EWC and EWT) were depicted in Fig. 2. The absence of C = C(1652 cm⁻¹) and the C-H stretching of the double C = C-H(3009 cm⁻¹) suggest that almost all C = C bonds in WCO had taken part in the epoxidation reaction. The new absorption peaks appeared 824 and 844 cm⁻¹ can be attributed to the epoxy group. The other peaks obtained from the spectra are: 726 cm⁻¹ (methylene, in-phase rocking), 1093 cm⁻¹ (ether, anti-symmetric stretch), 1174 cm⁻¹, 1245 cm⁻¹ (ester, anti-symmetric stretch), 1379 cm⁻¹ (methyl, symmetric deformation), 1463 cm⁻¹ (methyl, anti-symmetric deformation) and 1745 cm⁻¹ (esters, aliphatic C = O stretch). The olefinic hydrogens of WCO peaks at 5.30-5.42 ppm decreased and peaks at 3.05-3.15 ppm (protons of the epoxide ring, -CH-CH-) increased indicates that nearly all C = C bonds are converted to epoxide. The peaks at 5.24-5.28 ppm (methylene protons of backbone, -CH₂-CH₂-) and 4.11-4.31 ppm (four methylene protons of backbone, -CH₃-CH₂-) decreased, peaks at 3.95-4.03 ppm (CH proton of the O=C-O-CH₁-alkyl) appeared.

The assignment of signal is given as follows: δ 0.86-0.92 ppm (protons of terminal -CH₃), δ 1.23-1.37 (methylene protons, -(CH₂)ₑ), δ 1.56-1.67 ppm (protons of β-CH₂ to carbonyl), δ 2.20-2.24 ppm (protons of α-CH₂ to carbonyl), δ 2.87-3.01 ppm (protons of -CH₂ – adjacent to two epoxy group), δ 3.05-3.15 ppm (protons of the epoxide ring, -CH₂CH₂), δ 4.11-4.16 and 4.27-4.31 ppm (four methylene protons of backbone, -CH₂-CH₂), δ 5.24-5.28 ppm (methylene protons of backbone, -CH₂-CH₂).

2.4 Viscosity and viscosity index (VI)

Kinematic viscosities of the fluids were measured at 40°C and 100°C using SYP1003-IX Kinematic Viscometer Apparatus (Shanghai SK Petroleum & Chemical Equipment Co., Ltd; CHN). Viscosity and VI were calculated using the official ASTM D 445 and ASTM D 2270 methods, respectively. Duplicate measurements were made and average values were reported.
2.5 Pour point and cloud point

Pour point (PP) and cloud point (CP) were measured with Cloud Point & Pour Point Apparatus, SYP1022-III (Shanghai SK Petroleum & Chemical Equipment Co., Ltd; CHN) according to the ASTM D 97 and ASTM D 2500 methods. The PP was defined as the coldest temperature at which the sample still poured. It is a rough indication of the lowest temperature at which oil is readily pumpable. The cloud point is the temperature at which dissolved solids, such as paraffin wax, are no longer completely soluble, instead precipitating as a second phase giving the fluid a cloudy appearance. The cloud point indicates the tendency of oil to plug filters or small orifices at cold operating temperatures. All runs were carried out in duplicate and average values were reported.

2.6 Copper strip corrosion test

Determination of corrosiveness of the fluids was done using SYP1017-II Copper Strip Corrosion Tester (Shanghai, China) as per ASTM D 130 method. A polished Cu strip was immersed in 30 mL of the sample being tested at 100°C for 3 h. After 3 h, the Cu strip was removed, washed and the color and tarnish level were assessed against the ASTM Copper Strip Corrosion Stand.

2.7 Pressure differential scanning calorimetry (PDSC) test

PDSC test was performed using a computerized NETZSCH DSC 204-2 thermal analyzer (Bavarian, GER). Typically a 0.3-0.5 mg sample was taken in a hermetically sealed-type aluminum pan (produced by NETZSCH) with a pinhole lid for interactions of the sample with the reactant to ensure proper oil-air interaction and eliminate gas-diffusion limitations. High-purity oxygen was pressurized in the module at a constant pressure of 3.5 MPa (flow of 100 mL/min). Oxidation onset temperature (OOT) and oxidation induction time (OIT) (in minutes) were measured in the PDSC by the programmed temperature and isothermal modes, respectively.

For oxidation onset temperature (OOT) measurement, the samples were heated from ambient temperature to 350°C at a constant rate of 10°C/min. In isothermal methods for measuring oxidation induction time (OIT), the sample temperature was programmed to increase at a rate of 100°C/min from ambient temperature to 150°C followed by equilibration at this temperature. Subsequently, an iso-track segment of sufficient length (10-30 min) was maintained to observe the thermal transition. Each sample was run in triplicate and the average values were reported.

2.8 Rotating pressure vessel oxidation test (RPVOT)

Rotating pressure vessel oxidation determinations were performed on a RPVOT apparatus manufactured by Shanghai SK Petroleum & Chemical Equipment Co., Ltd (China) according to ASTM Method D 2272. Samples were measured to 50.0 ± 0.5 g with 5.0 mL of reagent water added to the sample. The copper catalyst was measured to 3 m and sanded with 220-grit silicone carbide sand paper. The wire was wound to have an outside diameter of 44-48 mm and a weight of 55.6 ± 0.3 g and to a height of 40-42 mm. The bomb was assembled and slowly purged twice with oxygen, and then charged with 90.0 ± 0.5 psi (620 kPa) of oxygen then tested for leaks by immersing in water. The pressure in the bomb was continuously recorded with time. The RBVOT time is the oxidative induction time (OIT) at which the pressure of the bomb has dropped by 25 psi (175 kPa). All samples were run in duplicate, and the average RPVOT times in minutes are reported.

2.9 Four-ball friction and wear test

The tribological tests were carried out on an MMW-10 four-ball machine manufactured by Jinan Shun Mao Test Instrument Co., Ltd. (China), according to ASTM D 4172-2011 method. The balls used in tests were obtained from Sinopec (China) and had the following specification: chrome alloy steel (AISI NO E52100), Grade 25 extra polish; diameter 12.7 mm; hardness of 64 to 66 Rockwell C. Prior to use in the tests, balls were degreased by consecutive 10 min ultrasonication in hexane solvents. All the anti-wear tests were conducted at a rotating speed of 1200 rpm and loads of 392 N, with duration of 60 min at 75°C. An optical microscope was used to determine wear scar diameters (WSD) of three lower balls with an accuracy of ±0.01 mm, and these diameters were averaged and cited as the WSD. Friction coefficients were automatically measured and recorded. In the friction and wear test, WSD and COF data were used to evaluate the oil. Lubricants with lower WSD and COF are preferred.

3 Results and Discussion

3.1 Viscosity and viscosity index (VI)

Viscosity is a key parameter for lubricant, which plays a fundamental role in lubrication. The viscosity of lubricating oil is extremely sensitive to the operating temperature and the viscosity index (VI) is developed to indicate the effect of temperature changes on the viscosity of the oil. The viscosities of nature vegetable oils exhibit relatively narrow viscosity range due to their triglycerides structure which hampered widespread industrial application. Therefore, it is essential to develop bio-based lubricant over a moderate range of viscosity from the vegetable oils or similar materials. The viscosity at 40 and 100°C and VI of chemically modified WCO and neat WCO are listed in the Table 1. For the purposes of comparison, viscosity and VI values for fresh soybean oil (SBO) is also included in Table 1. WCO displayed the kinematic viscosities of 36.7 and 8.5 cSt at 40 and 100°C, respectively. The viscosity values of WCO are
slightly higher than SBO, which suggests that the polymerization reactions take place during the usage and resulting in the viscosity increase of the oil. Viscosities of the chemically modified WCO range from 15.9 to 43.4 cSt at 40°C, and from 3.4 to 7.4 cSt at 100°C with the increase of chain length of alkoxy group on the bio-lubricants which suggests that chemical modification can broaden the viscosity range of WCO. It’s worth to note that the chemical modification causes a drastic VI decrease of the WCO from 220 to approximately 135 for EWT. The VI varies with the molecular structure of the lubricant, and in the order of EWO (157) > EWC (142) > EWT (135). Although the VI is lower than WCO and SBO, the synthesized bio-lubricants still exhibit good viscosity-temperature properties (with the VI higher than 120) than conventional mineral oils and can be considered as high performance bio-lubricants.

3.2 Low temperature properties

It is well recognized that poor low temperature flow property is another obstacle which limits large scale application of the triglycerides oils based lubricants. As shown in Table 1, both WCO (PP = −2°C and CP = 4°C) and SBO (PP = −8°C and CP = 0°C) present a pour point above −10°C, which is much higher than their mineral oil counterpart. This can be explained that triglycerides based oils (WCO and SBO) have a tendency to form macro crystalline structures at low temperature through uniform stacking of the “bend” triglyceride backbone and such macro crystals limit the easy flow of the fluid due to loss of kinetic energy of individual molecules during self-stacking. Transforming glycerol group in vegetable oils to other branching alkoxy groups can initiate the corrosion of metal surfaces and even produce rust.

| Sample | Kinematic viscosity (cSt) | Viscosity index (VI) | Cloud point (°C) | Pour point (°C) | Copper strip corrosion (100°C, 3h) | Total acid number (TAN, mgKOH/g) |
|--------|---------------------------|----------------------|------------------|----------------|-----------------------------------|----------------------------------|
| WCO    | 36.7 @ 40°C, 8.5 @ 100°C | 220                  | 4                | −2             | 1b                                 | 1.56                             |
| SBO    | 31.5 7.65                 | 227                  | 0                | −8             | 1a                                 | 0.54                             |
| EWO    | 15.9 3.4                  | 157                  | −15              | −17            | 1a                                 | 0.27                             |
| EWC    | 24.7 5.1                  | 142                  | −18              | −20            | 1a                                 | 0.55                             |
| EWT    | 43.4 7.4                  | 135                  | −21              | −24            | 1a                                 | 0.37                             |

3.3 Corrosion resistance property

Corrosion behavior of WCO and its derivatives (EWO, EWC and EWT) were performed with copper-strip corrosion tester. As depicted in Table 1, chemically modified WCOs show slightly corrosion (1a) on Cu strip whereas WCO has a marked corrosion (1b) effect on Cu strip. The corrosion of Cu strip with WCO may be due to the presence of a high free fatty acid (FFA). The high content of FFA was generated during frying and eventually increased the total acidity of the oil. Lubricants with high acidity have a negative influence on rubber sealing parts and paints and can initiate the corrosion of metal surfaces and even produce rust.

3.4 Thermo-oxidative stability

The oxidation stability of SBO, WCO and WCO based bio-lubricants (EWO, EWC and EWT) were evaluated with isothermal PDSC, programmed temperature PDSC, and RPVOT methods. These oxidation stability tests are widely used in the lubricant industry and are considered reliable for base oil as well as finished lubricants. The isothermal PDSC method is a test method widely used for determining oxidation stability of petroleum products, and is finding popularity for testing oxidative stability of bio-based lubricant as well. The isothermal PDSC test results of WCO, SBO, EWO, EWC, and EWT are shown in Fig. 4. The neat WCO shows the worst oxidation stability with an oxidation induction time (OIT) of only 3.5 min. This
can be explained by the existence of abundant unsaturated double bond in the molecule along with the primary oxidation impurities generated during the usage, both of which are more prone to cause oxidation. The fresh SBO also showed a low OIT of 5.7 min, as was typical for vegetables oils. However, derivatives (EWO, EWC and EWT) of WCO display excellent thermo-oxidative stability under the same conditions as compared to the WCO and SBO. The OIT of EWO, EWC and EWT are 79.2, 50.4, and 35 min, respectively. The most striking result is achieved by EWO for 79.2 min, with more than 20 times improvement than untreated WCO. The excellent oxidative stability of chemically modified WCO can be attributed to the successful removal of polyunsaturation (by epoxidation), which results in the improvement of the oxidation stability of the lubricant.

3.4.2 Programmed temperature PDSC method

Programmed temperature PDSC method was used to study the effect of temperature on the samples through the determination of the oxidation onset temperature (OOT)\(^{25}\). The OOT is the temperature at which a rapid increase in the rate of oxidation is observed. A high OOT suggests a high oxidation stability of the oil\(^{25, 27}\). The results of WCO and its derivatives are presented in Fig. 5. According to the experimental data, the WCO and SBO suffer an expected low OOT result of 121.2°C and 141.5°C, respectively, due to the presence of active \(-\mathrm{C} = \mathrm{C}\)– bonds in the fatty acid of triglycerides. The removal of unstable carbon-carbon double bonds in the WCO by converting them into epoxy groups significantly enhances the thermal and oxidative stability of the oil. The OOT of epoxidized fatty acid branched alcohol esters followed the order EWO(194.5°C) > EWC(180.3°C) > EWT(163.9°C). The thermo-oxidative stability tendency of the synthesized lubricants in Fig. 3 and Fig. 4 indicate that longer alkyl chains derivatives have more accessible sites that are prone to oxidation, which makes them more susceptible to cleavage than shorter chains.

Fig. 3 Comparison of the \(^1\)H NMR spectra of the WCO and synthesized bio-lubricants (EWO, EWC and EWT).

Fig. 4 Isothermal PDSC results for WCO, SBO and chemical modified WCO derivatives.
3.4.3 Rotating Pressure Vessel Oxidation Test (RPVOT).

Figure 6 shows the RPVOT results of different lubricants. As shown in the Fig. 6, the synthesized bio-lubricants exhibit enhanced oxidative stability than WCO. The OIT of EWO, EWC and EWT are 127.4, 92.9, and 69.8 min, respectively, which is much higher than WCO (11 min). This result is expected since epoxidation on the \(-\text{C} = \text{C}\)-bonds have removed the highly reactive unsaturation site. The new molecules are free of reactive double bonds and much more stable than the neat WCO. Moreover, the RPVOT results are in good agreement with the PDSC test and suggest that there is a good correlation between the two test methods.

3.5 Tribology properties

The friction-reducing and anti-wear tests of WCO and its derivatives were conducted using four-ball friction and wear machine and the results were listed in Table 2. It can be found in the table that WCO present a wear scar diameter of 0.61 mm and an average friction coefficient of 0.065. As for the developed bio-lubricants, the WSD values decreased with the increase of alkyl chain. The trend for the COF of the lubricants is similar: EWO > EWC > EWT. It’s worth to mention that EWC and EWT exhibit improved anti-wear and friction reducing properties than WCO.

4 Conclusions

Bio-lubricant base fluids (EWO, EWC and EWT) were successfully synthesized by epoxidation using \( \text{H}_2\text{O}_2 \), transesterification with methanol and followed by branched alcohols (isooctanol, isotridecanol and isooctadecanol). Based on the results obtained it can be concluded that developed bio-lubricants have excellent oxidation stability and exhibit good viscosity-temperature properties. All the synthesized bio-lubricants performed much better low temperature properties than WCO. Furthermore, the copper strip corrosion experiments revealed a better anti-corrosion property of bio-lubricants than that of WCO. Tribological investigations suggested that EWC and EWT showed improved tribological performance than WCO. The experimental results indicate that chemically modified WCO are economical, sustainable, and eco-friendly alternatives for mineral oils and will find potential practical application in the field of lubrication.

Acknowledgment

The authors gratefully acknowledge the financial support of the National “973” Program of China (Grant No. 2013CB632301), Innovation Fund for Technology Based Firms. (Grant No.12C26213714170) & Qingdao Laoshan Science & Technology Bureau, China (Grant No. LS-12-KJ2-37).
References

1) Nagendramma, P.; Kaul, S. Development of ecofriendly/biodegradable lubricants: An overview. *Renew. Sustain. Energy Rev.* **16**, 764-774 (2012).

2) Betton, C. I. Lubricants and Their Environmental Impact. In Chemistry and Technology of Lubricants; Mortier RM, Fox MF, Orszulik ST, Eds.; Springer: The Netherlands (2010).

3) Salimon, J.; Salih, N.; Yousif, E. Biolubricants: Raw materials, chemical modifications and environmental benefits. *Eur. J. Lipid. Sci. Technol.* **112**, 519-530 (2010).

4) Hahn, S.; Dott, W; Eisentraeger, A. Characterization of ageing behavior of environmentally acceptable lubricants based on trimethylolpropane esters. *J. Synth. Lubr.* **23**, 223-236 (2006).

5) Pettersson, A. Tribological characterization of environmentally adapted ester based fluids. *Tribol. Int.* **36**, 815-820 (2003).

6) Hashem, A. I.; Bonga, E.S. I.; Salem, A. E.; El-Kasaby, M.; El-Nahas, A. M. Conversion of some vegetable oils into synthetic lubricants. *Energy Sources Part A* **35**, 397-400 (2013).

7) Salimon, J.; Salih, N.; Yousif, E. Improvement of pour point and oxidative stability of synthetic ester basestocks for biolubricant application. *Arab. J. Chem.* **5**, 193-200 (2010).

8) Adhvaryu, A.; Erhan, S. Z. Epoxidized soybean oil as a potential source of high-temperature lubricants. *Ind. Crops Prod.* **15**, 247-254 (2002).

9) Hwang, H. S; Erhan, S. Z. Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point. *J. Am. Oil Chem. Soc.* **78**, 1179-1184 (2001).

10) Kurth, T. L.; Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Adsorption behavior of epoxidized fatty esters via boundary lubrication coefficient of friction measurements. *Chem. Eng. Commun.* **194**, 1065-1077 (2007).

11) Vlek, T.; Petrovic, Z. S. Optimization of the chemoenzymatic epoxidation of soybean oil. *J. Am. Oil Chem. Soc.* **83**, 247-252 (2006).

12) Moser, B. R.; Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Diester from oleic acid: synthesis, low temperature properties, and oxidation stability. *J. Am. Oil Chem. Soc.* **84**, 675-680 (2007).

13) Gryglewicz, S.; Piechocki, W.; Gryglewicz, G. Preparation of polyol esters based on vegetable and animal fats. *Bioresour. Technol.* **87**, 35-39 (2003).

14) Akermana, C. O.; Gabera, Y.; Ghanid, N. A.; Lamsae, M.; Hatti-Kaul, R. Clean synthesis of biolubricants for low temperature applications using heterogeneous catalysts. *J. Mol. Catal. B: Enzym.* **72**, 263-269 (2011).

15) Honary, L. A. T. An investigation of the use of soybean oil in hydraulic systems. *Bioresource Technol.* **56**, 41-47 (1996).

16) Glancey, J. L.; Knowlton, S.; Benson, E. R. Development of a high oleic soybean oil-based hydraulic fluids. *SAE Technical Paper* (1995).

17) Cannon, G. S.; Honary, L. A. T. Soybean based transformer oil and transmission line fluid. *US patent 6245726* (2001).

18) Nagendramma, P.; Kaul, S.; Bisht, R. P. S.; Tyagi, M. R. Development of biodegradable lubricating oil formulations from nonedible vegetable oils. In: *101st AOCS annual meeting & expo* (2010).

19) Yaakob, Z.; Mohammad, M.; Alherbawi, M.; Alam, Z; Sopian, K. Overview of the production of biodiesel from Waste cooking oil. *Renew. Sustain. Energy Rev.* **18**, 184-193 (2013).

20) Patil, P. D.; Gude, V. G.; Deng, S. Biodiesel production from jatropha curcas, waste cooking, and camelina sativa oils. *Ind. Eng. Chem. Res.* **48**, 10850-108056 (2009).

21) Wang, E. P.; Ma, X.; Tang, S. Z.; Yan, R.; Wang, Y.; Rily, W. W.; Reaney, M. J. T.; Synthesis and oxidative stability of trimethylolpropane fatty acid triester as a biolubricant base oil from waste cooking oil. *Biomass Bioenergy* **66**, 371-378 (2014).

22) Chowdhury, A.; Mitra, D.; Biswas, D. Biolubricants synthesis from waster cooking oil via enzymatic hydrolysis followed by chemical esterification. *J. Chem. Technol. Biotechnol.* **88**, 139-144 (2013).

23) Pavía, D. L.; Lampman, G. M.; Kriz, G. S. Introduction to Spectroscopy. United States: Thomson Learning, Inc. 4th ed. (2009).

24) Hwang, H. S.; Adhvaryu, A.; Erhan, S. Z. Preparation and properties of lubricant basestocks from epoxidized soybean oil and 2-ethylhexanol. *J. Am. Oil Chem. Soc.* **80**, 811-815 (2003).

25) Sharma, B. K.; Stipanovic, A. J. Development of a new oxidation stability test method for lubricating oils using high-pressure differential scanning calorimetry. *Thermochimica Acta* **402**, 1-18 (2003).

26) Wu, Y. X.; Li, W., M.; Zhang, M.; Wang, X. B. Improvement of oxidative stability of trimethylolpropane triolite lubricant. *Thermochimica Acta* **569**, 112-118 (2013).

27) Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresour. Technol.* **99**, 7333-7340 (2008).