Chemically modified *Jatropha curcas* oil for biolubricant applications

Nurazira Mohd Nor[1], Nadia Salih[2] and Jumat Salimon[2]

[1]*School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 72000 Kuala Pilah, Negeri Sembilan, Malaysia*
[2]*Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

Abstract

Jatropha curcas oil is one of interesting renewable resources for preparation of biolubricants. However, direct application of this oil as a biolubricant is restricted due to its low oxidative stability. This drawback can be overcome by molecule structural redesign through a chemical modification process at its unsaturated functional groups. *Jatropha curcas* oil was modified *via* epoxidation, ring opening and esterification processes. Its conversion to the epoxidized oil was performed by using *in situ* performic acid as a catalyst, then reaction with oleic acid in the presence of *p*-toluenesulfonic acid as a catalyst in the ring opening process. The final esterification process with oleic acid was catalyzed by sulfuric acid. Molecular structures of the modified oil were determined by measurements of the oxirane oxygen content and by Fourier-transform infrared (FTIR), proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectroscopy analyses. The results showed that the oxidative stability, viscosity, flash point and pour point of the final product were significantly improved. In specific, the ring opening and esterification processes inducing branching and bending in the final oil molecular structure have resulted in the improved viscosity index of 135, the pour point of -29 °C and the increased flash point of 250 °C.

Keywords: epoxidation; ring opening; esterification; oleic acid; green biolubricant.

Available on-line at the Journal web address: http://www.ache.org.rs/HI/

ORIGINAL SCIENTIFIC PAPER

UDC: 665.345.5:621.892.8:677.027.622:66.094.39

Hem. Ind. **75 (2)** 117-128 (2021)

1. INTRODUCTION

In the last decade, a variety of new technologies have emerged aiming at development of products from renewable sources. to the reason is in increasing concerns over the use of petroleum-based products, which causes progressive reduction of fossil fuel reserves and has negative impacts on the environment [1,2]. In the field of the use of lubricant, there are wide ranges of lubricant base oils, which include mineral, synthetic, re-refined and plant oils. Among these, mineral oils are the most commonly used [3]. Mineral oils are more stable and readily available than natural oils and exhibit a wider range of viscosities [2]. However, they pose a constant threat to ecology and ground water reserves due to their inherent toxicity and non-biodegradable nature [3,4]. Reduction of petroleum oil resources and increasing greenhouse gas emissions give a clear picture of the importance of the move towards sustainable development [5] where the use of renewable sources in industry is vital. Such examples are studies on plant oils as a feedstock in the manufacture of products for daily use. Plant oils are found to be the best alternative source not only because they are renewable raw materials, but also because they are biodegradable and non-toxic [3,6], unlike conventional mineral based oils [2]. Plant oil-based biolubricants such as *Jatropha curcas* (*J. curcas*) oil and its derivatives have excellent lubricity and biodegradability properties for which they are being more closely examined as a base stock for lubricants and functional fluids [7,8]. Also, these oils exhibit high viscosity index [9]. However, plant oils, particularly *J. curcas* oil have several disadvantages including instability that limit their applications in biolubricant industries. Plant oil formulations provide many challenges such as low oxidative stability [2,10] and poor low temperature properties [5,11].

Corresponding author: Nadia Salih, Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
E-mail: nadiaalnami@hotmail.com
Paper received: 09 August 2020
Paper accepted: 09 March 2021
https://doi.org/10.2298/HEMIND200809009N

This is due to the presence of the weakest track of double bonds present in the unsaturated fatty acid structure [11,12] and instable β-hydrogen at glycerol backbone in the oil triacylglycerol molecule structure.

Many studies have reported production of *J. curcas* oil based biolubricants by improving the oxidative stability by the replacement of the glycerol backbone with polyhydric alcohols. Esterification or transesterification with polyhydric alcohols, especially with trimethylopropanol (TMP) in particular, are well documented. Some studies reported production of *J. curcas* biolubricants *via* esterification of the fatty acid methyl ester (FAME) and TMP [13-17] and direct transesterification of the oil with TMP [18]. Biolubricants based on the *J. curcas* oil showed varied properties depending on the production method. Utilization of 1 % $NaOCH_3$ as a catalyst resulted in 47% yield with a pour point (PP) of -3 °C and viscosity index (VI) of 178–183 [19]; use of 2 % $HClO_4$ has yielded 70 % with PP of -23 °C, flash point (FP) >130 °C and VI of 150 [20]; use of 0.9 % $NaOCH_3$, resulted in 98.2 % yield with PP of -3 °C, FP of 273 °C and VI of 140 [21]; finally the use of a calcium hydroxide catalyst produced a biolubricant with PP of −12 °C, FP of 178 °C and VI of 204 [22].

Scientific approaches have yet to be taken to improve the oxidative stability and low-temperature properties. With this aim, chemical modification of the *J. curcas* oil molecule structure can be carried out. The oil triacylglycerol structures have different functional sites and groups such as double bonds and allylic carbon, which are potential sites for chemical modification [23]. Double bonds present the weakest track being reactive and allowing addition of functional groups in fatty acids. Epoxidation is one of the most important functionalization reactions of double bonds to obtain stable functional groups in order to improve the plant oil oxidative stability [2,8,24].

Epoxidation of *J. curcas* oil using peracids is one of the most important steps and a useful modification process acting on double bonds since epoxides are reactive intermediates that can be converted into other functional groups by ring-opening reactions [25]. The oxirane ring opening by acidic or alkaline catalyzed reactions with a suitable reagent produces interesting poly-functional compounds [8,27] whereas reduction of the oil structural uniformity by attaching alkyl side chains would improve the low-temperature performance [8,26]. In general, plant oils with high contents of unsaturated fatty acid are used to produce high epoxy functionality materials [27]. Products obtained from epoxides can be used as high-temperature biolubricants, while the products obtained from ring opening can be used as low-temperature biolubricants [12]. Non-edible plant oils such as *J. curcas* oil have been studied as a better alternative source and more suitable in different industries such as biolubricant production [28].

However, until now modification of *J. curcas* oil was not attempted by reactions on double bonds or the unsaturated functional groups. Therefore, in this paper, we report the modification process by manipulation and making use of the oil unsaturated functional groups in the forms of oleyl and linolioyel which are present in J. *curcas* oil triacylglycerols. To enhance the lubrication properties, *J. curcas* oil was converted into the epoxidized oil followed by the oxirane ring opening and finally esterification reactions with oleic acid.

1. MATERIALS AND METHODS

1. 1. Materials

J. curcas seed was obtained from a Plant House Plot at the Universiti Kebangsaan Malaysia and extracted using the Soxhlet extraction method. Oleic acid (90 %) was purchased from Sigma Aldrich (USA). Ethyl acetate, toluene, sodium hydrogen carbonate and sodium chloride were purchased from Systerm (Malaysia). Formic acid (88 %) was obtained from Fisher Scientific (USA) and hydrogen peroxide 30% from Merck, Germany. All chemicals and solvents were either analytical grade or high performance liquid chromatography (HPLC) and used directly without further purification.

1. 2. Epoxidation reaction

The epoxidation process of *J. curcas* oil (JCO) was carried out according to Jumat *et al.* [29]. The molar ratio of double bonds in JCO to HCOOH to H_2O_2 was 1:1:2.5 and 100 g oil samples were used. JCO and formic acid were weighed and placed into a 250 cm^3 three neck round bottom flask, which was heated to 45 – 55 °C and continuously stirred by using a magnetic stirrer. When the temperature reached 40 °C, H_2O_2 was added slowly. The reaction was continued for 2.5 h with vigorous stirring of 900 rpm. At the end of reaction, the product was neutralized with sodium hydrogen carbonate solution, sodium

chloride solution and distilled water. The product, epoxidized *J. curcas* oil (EJCO), was kept overnight by adding anhydrous sodium sulfate to remove water. Then, the product was filtered using Whatmann No. 1 filter paper (Whatmann, Germany).

1. 3. Ring opening reaction

In the ring opening reaction [29,30], the mole ratio of EJCO and oleic acid was 1: 3. The EJCO and oleic acid were added to a 250 cm^3 three-neck round bottom flask and heated at 70 °C to 80 °C for 15 min. Then, 1 % of *p*-toluenesulfonic acid (PTSA) was added to yield the concentration of 1 wt.%. The reaction was carried out for 6 h at 100 – 140 °C at continuous stirring of 900 rpm using a magnetic stirrer. At the end of reaction, the product was neutralized with sodium hydrogen carbonate solution, sodium chloride solution and ethyl acetate. The product was kept overnight with the addition of anhydrous sodium sulfate. The product, *J. curcas* oil tetraester (JCOT), was filtered by using Whatmann No. 1 filter paper followed by solvent evaporation by using a rotary evaporator at 70 °C.

1. 4. Esterification reaction

In the esterification reaction [29], the mole ratio of the *J. curcas* oil tetraester (JCOT) and oleic acid was 1:3. The JCOT, oleic acid and sulfuric acid in 2 wt.% final concentration were added to a 500 cm^3 three-neck round bottom flask. 100 mL of toluene was added into the flask and the flask was connect to a Dean - Stark apparatus and a condenser and then heated in silicone oil. The esterification reaction was carried out at the temperature of 110-130 °C for 7-8 h. Once the reaction completed, the product was transferred into a separating flask and allowed to cool at room temperature. The product was neutralized with sodium hydrogen carbonate solution, sodium chloride solution and ethyl acetate to achieve pH of 6 - 7. The final product, *J. curcas* oil octaester (JCOO) was kept overnight with the addition of anhydrous sodium sulfate followed by filtration by using a Whatmann No. 1 filter paper and solvent evaporation by using a rotary evaporator at 70 °C. The esterification processes were repeated at least for three times.

1. 5. Structural characterizations

Formation of EJCO, JCOT and JCOO was confirmed first by using Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Perkin Elmer Infrared Spectrophotometer (USA) in the range 400-4000 cm^{-1}. Nuclear magnetic resonance spectroscopy (NMR) was carried out to confirm the molecular structure of all products. ^1H and ^{13}C NMR were recorded on a JEOL-ECP 400 spectrometer (Japan) at 400 MHz ^1H/100.61 MHz ^{13}C using $CDCl_3$ as a solvent.

1. 6. Determination of the oxygen oxirane content

Evolution of the epoxidation reaction was monitored by measuring the oxygen oxirane content (OOC) in accordance with the official and recommended practice of AOCS Cd 9-57 [31]. Under the prescribed conditions of this method, oxygen was titrated directly using a hydrobromic acid solution in glacial acetic acid. From the OOC measurement, the relative conversion to oxirane (RCO) value was calculated by the following formula:

$$\mathrm{RCO}=\frac{\mathrm{OOC_{exp}}}{\mathrm{OOC_{the}}}100 \quad (1)$$

where OOC_{exp} is the experimentally determined oxirane oxygen and OOC_{the} is the theoretical maximum oxirane oxygen. These parameters were calculated according to eqs (2) and (3), respectively, as:

$$\mathrm{OOC_{exp}}=\frac{1.60VN}{Wt} \quad (2)$$

where *V* and *N* are the volume and normality of the HBr solution and *Wt* is the weight of the sample.

$$\mathrm{OOC_{the}}=\frac{IV_O/2A_\mathrm{i}}{100+\left(IV_O/2A_\mathrm{i}\right)A_\mathrm{O}}A_\mathrm{O}100 \quad (3)$$

where A_i (126.9) and A_o (16.0) are the atomic masses of iodine and oxygen, respectively and IV_o is the initial iodine value of the sample.

1. 7. Determination of the pour point

The lowest temperature at which a liquid can still be poured (still behaves like a fluid) is called the pour point (PP), which is used for investigation of the fluid flow behavior at low temperatures. The ASTM D97-17 method [32,33] was used to measure the PP of the biolubricants in this study, with some modifications. A U-tube and an attached thermometer were used in the experimental setup, with a temperature range of -80 to 0 °C. About 10 cm^3 of the sample was placed in the U-tube and the sample was placed in a freezer (at -80 °C). The sample (held inside the U-tube in a horizontal position) was left in the freezer for 24 h to ensure freezing [34]. Once frozen (after 24 h), the sample was taken out from the freezer and slowly thawed at room temperature monitoring for the start of the flow. The temperature measured at this point denotes the pour point. The pour point test was done in triplicate.

1. 8. Determination of the flash point

The lowest temperature at which a heated volatile liquid vaporizes and ignites is called the flash point (FP). The ASTM D 56-79 method was used to determine the flash point of the biolubricants in this study, using a Tag Closed Tester [33]. A 0 to 500 °C range thermometer was used for the test. First, a test cup was prepared, and approximately 10 cm^3 of the test specimen was filled into it. As a precaution due to using remarkably high temperatures, the flash point test was carried out in a fume chamber. At first, the heat was applied to the product rapidly increase the temperature to 100 °C. Then, the heating was slowed to a constant rate of 5 °C/min nearing the flash point. A spark plug with a test flame was passed across the cup at specified intervals. The lowest liquid temperature at which the vapor of the test specimen was ignited by the test is known as the flash point and the test was performed in triplicate.

1. 9. Determination of viscosity and the viscosity index

A good biolubricant should have a moderate viscosity index **(**VI). The VI value indicates the change in kinematic viscosity of a biolubricant with a change in temperature. Essentially, the VI indicates the quality of the biolubricant and the automotive industry uses this index to characterize lubricating oils. Kinematic viscosities of the biolubricants in this study were measured by using a rheometer model MCR 301, Anton Paar Instruments (Germany). The standard method ASTM D 2270-04 was used to calculate the viscosity and the viscosity index [33]. A hot plate heater was set to 40 and 100°C and the sample (1 cm^3) was added [37]. Then, the VI was determined by using the formula:

$$IV = \frac{L-U}{L-H}100 \quad (4)$$

where U is the kinematic viscosity at 40 °C of the oil sample (cSt), L is the kinematic viscosity at 40 °C of an oil with a zero-viscosity index having the same kinematic viscosity at 100 °C as the oil sample (cSt), H is the kinematic viscosity at 40 °C of an oil with a viscosity index 100, having the same kinematic viscosity at 100 °C as the oil sample (cSt).

1. 10. Determination of oxidative stability

The lubricant oil oxidizes faster when it is exposed to oxygen at elevated temperatures, which reduces the oil quality as it becomes more viscous. Pressure differential scanning calorimetry (PDSC) (model DSC822e Metter Toledo, Switzerland) was used to determine the oxidative stability temperature (OST) of the oil. Typically, a 2 µL sample resulting in a film thickness of less than 1 mm, was placed in an aluminium pan, which was hermetically sealed with a pinhole lid and oxidized in the presence of dry air (Gateway Airgas, St. Louis, MO), which was pressurized in the module at a constant pressure of 1378.95 kPa (200 psi). A 10 °C min^{-1} heating rate from 50 to 350 °C was used during each experiment. The oxidation stability temperature (OST) was calculated from the plot of the heat flow versus temperature for each experiment [35,38]. The OST test was performed in triplicate.

2. RESULTS AND DISCUSSION

2. 1. Epoxidation and ring opening reactions

In the epoxidation process, one oxygen atom will be attached to the active site of unsaturated double bonds to form an epoxide ring. Atomic oxygen from the oxygen donor was transferred to a position far from the carbonyl functional group. Performic acid was formed *in situ* after formic acid reacted with hydrogen peroxide (H_2O_2), which acts as an oxygen donor while formic acid as the active oxygen carrier [39]. Epoxidation of *J. curcas* oil (JCO) was successfully carried out to produce the epoxidized *J. curcas* oil (EJCO) with 87 % (w/w) yield. The OOC value was determined so to confirm the presence of oxirane oxygen ring in EJCO. The obtained OOC value was 4.92 while the theoretical value was 5.99. Based on both values, the relative conversion of oxirane oxygen in the epoxidation process is 82 %. The obtained EJCO was then submitted to the ring opening reaction with oleic acid to produce *J. curcas* oil tetraesters (JCOT). The average yield of the ring opening product was 68%. The ring opening process was monitored by the OOC value, which should be decreased as much as possible as the OOC reduction is proportional to the number of opened epoxide rings. The OOC value obtained after the ring opening process was significantly low approaching zero. A significant difference was observed between the OOC values of EJCO and JCOT and thus it is confirmed that all epoxide rings were successfully opened during the reaction with oleic acid. Further esterification of JCOT with oleic acid produced the final product *J. curcas* oil octaesters (JCOO) with the average yield of 64 %. Figure 1 shows the overall schematic reaction pathways in this research represented by dominant triacylglycerols (TAG) of 1-palmitoyl-2,3-dilinoleoyl-glycerol (PLL) found in JCO.

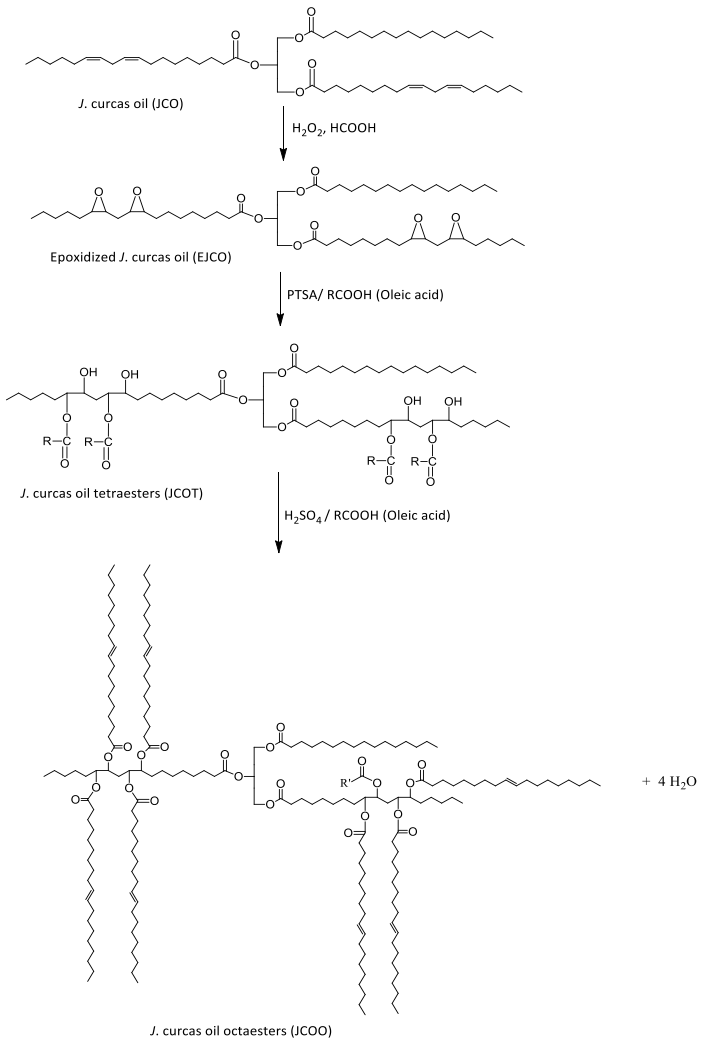

Fig 1. Schematic presentation of reactions used for modification of J. curcas oil

2. 2. FTIR spectra analysis

Presence of functional groups in all products was identified by using FTIR spectroscopy. Figure 2 shows the FTIR spectra of JCO, EJCO, JCOT and JCOO. The C=C olefin peak originates from the linolate acyl group, which was initially present in JCO appearing at 3007 cm^{-1} and was successfully converted into the epoxide ring. This is evidenced by the presence of the epoxide (oxirane) peak at 826 cm^{-1} in the EJCO spectrum. This value agrees with the literature reporting the wave number for the epoxide group in the range between 815-950 cm^{-1} [40]. Disappearance of the epoxide peak in the JCOT spectrum indicated that all epoxide rings have been successfully converted to hydroxyl ester functional groups in JCOT during the ring opening reaction with oleic acid. This is evidenced by the increase in the intensity of the peaks of the hydroxyl (OH) functional group at 3470 cm^{-1} and ester carbonyl C=O stretching at 1741 cm^{-1} in the JCOT spectrum. This agrees literature reports in which the wave number for the C=O ester group ranges from 1730-1750 cm^{-1} [40]. A significant change during the ring opening reaction is evidenced by the existence of a C=C olefin peak at 3005 cm^{-1} of oleate acyl group. Success of the final esterification reaction was evidenced by the reduction in peak intensity of the hydroxyl group at 3470 cm^{-1}, followed by an increase in the peak intensity of olefinic functional group at the wavenumber of 3005 cm^{-1} in the JCOO spectrum. The increase in the olefin (alkene) peak intensity showed that oleic acid has successfully reacted with the hydroxyl group and formed a big structure with branching esters.

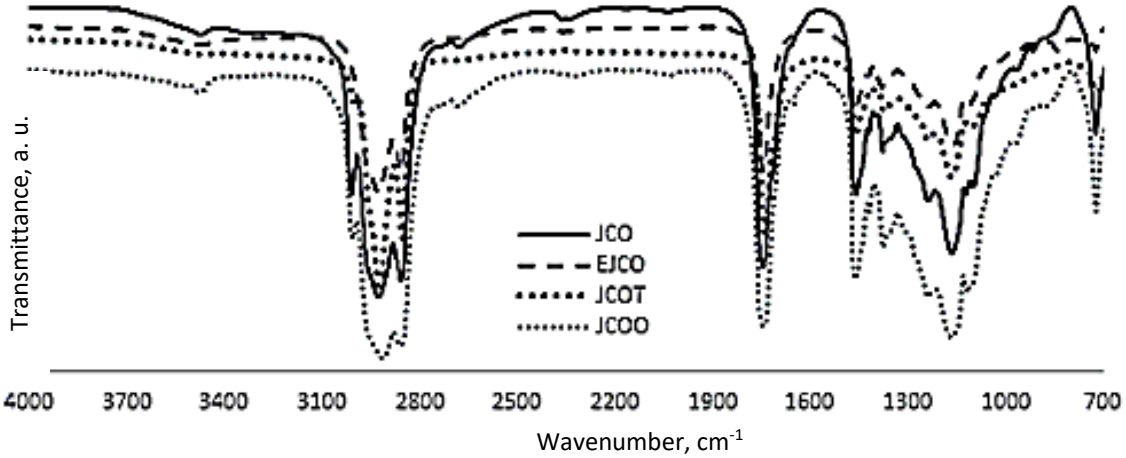

Figure 2. FTIR spectra of JCO, EJCO, JCOT and JCOO

2. 3. NMR spectra analysis

The epoxidation process (EJCO) can be proved by disappearances of the olefin proton at 5.340-5.311 ppm (C=C-H) and methylene proton at 2.029-1.975 ppm (-CH_2 methylene) which were initially present in the ^{1}H NMR JCO spectrum [41]. They are replaced by a peak at 3.013-2.863 ppm which corresponds to protons of oxirane ring (CHOCH) in the EJCO ^{1}H NMR spectrum. Result of the ring opening reaction can be confirmed by the disappearance of the peak of oxirane ring proton (CHOCH) in the ^{1}H NMR JCOT spectrum. Table 1 shows chemical shifts in ^{1}H NMR spectra for the JCO, EJCO, JCOT and JCOO.

Table 1. ^{1}H NMR chemical shifts of JCO, EJCO, JCOT and JCOO

Compound	Chemical shift, ppm	Remarks
JCO	5.340, 5.311	C=C-H
	2.319, 1.989, 1.615	-C-H_2 methylene
EJCO	3.013, 3.001, 2.863	CHOCH (oxirane ring)
JCOT	5.315	C=C-H
	2.311, 2.018	-C-H_2 methylene
	4.892	C-O-H
JCOO	5.334, 5.319, 5.304	C=C-H
	2.315, 2.017	-C-H_2 methylene
	4.892	C-O-H

Furthermore, the existence of hydroxyl group, which was formed during the ring opening reaction can be also confirmed by the existent peak for the hydroxyl proton at 4.89 ppm (C-O-H) in the JCOT spectrum. The existence and increase in the number of alkene groups due to further esterification by oleic acid can be evidenced by the existence of alkene C=C-H peak and methylene proton of $-CH_2$ in the JCOO spectrum. The spectrum also shows disappearance or a decrease in the hydroxyl group signal (C-O-H) in the JCOO spectrum [42].

The conversion of double bonds to oxirane ring can be proved by the disappearance of chemical shifts of olefin (C=C) at 130.217- 127.939 ppm, which initially existed in the ^{13}C NMR JCO spectrum and were replaced by chemical shifts at 57.159- 54.146 ppm, which represent the epoxy carbon atoms (C-O) in the ^{13}C NMR EJO spectrum. Results of the ring opening process can be evidenced by the disappearance of epoxy carbon and the existence of carbon olefin (C=C) at 130.240-129.759 ppm as well as the existence of peak at 73.590 ppm, which represents the carbon C-O next to the hydroxyl group in the ^{13}C NMR JCOT spectrum. The final product showed disappearance of the chemical shift of hydroxyl group and an increase in the intensity of carbon olefin (C=C) signal at 130.271-129.766 ppm in the ^{13}C NMR JCOO spectrum [43]. Table 2 shows chemical shifts in ^{13}C NMR spectra for JCO, EJCO, JCOT and JCOO. Figures 3 and 4 show ^{1}H and ^{13}C NMR spectra for JCO, EJCO, JCOT, and JCOO, respectively.

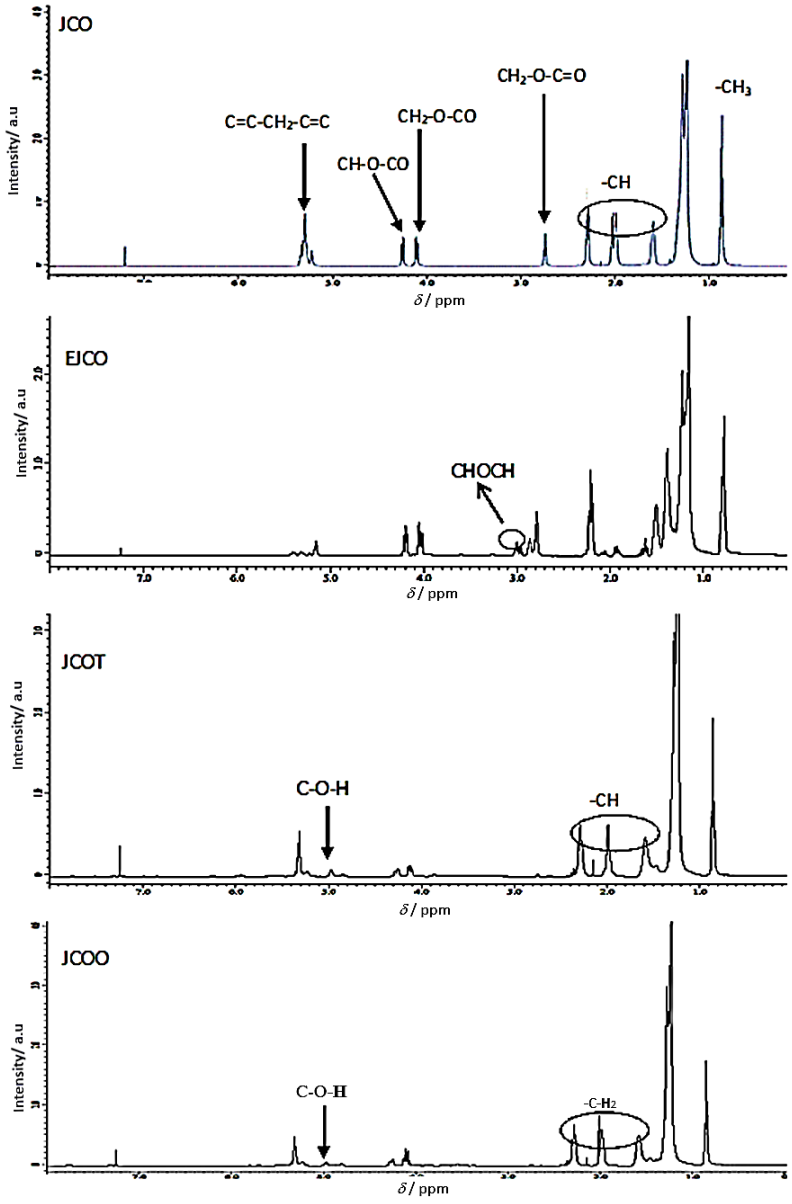

Figure 3. ^{1}H NMR spectra of JCO, EJCO, JCOT, and JCOO

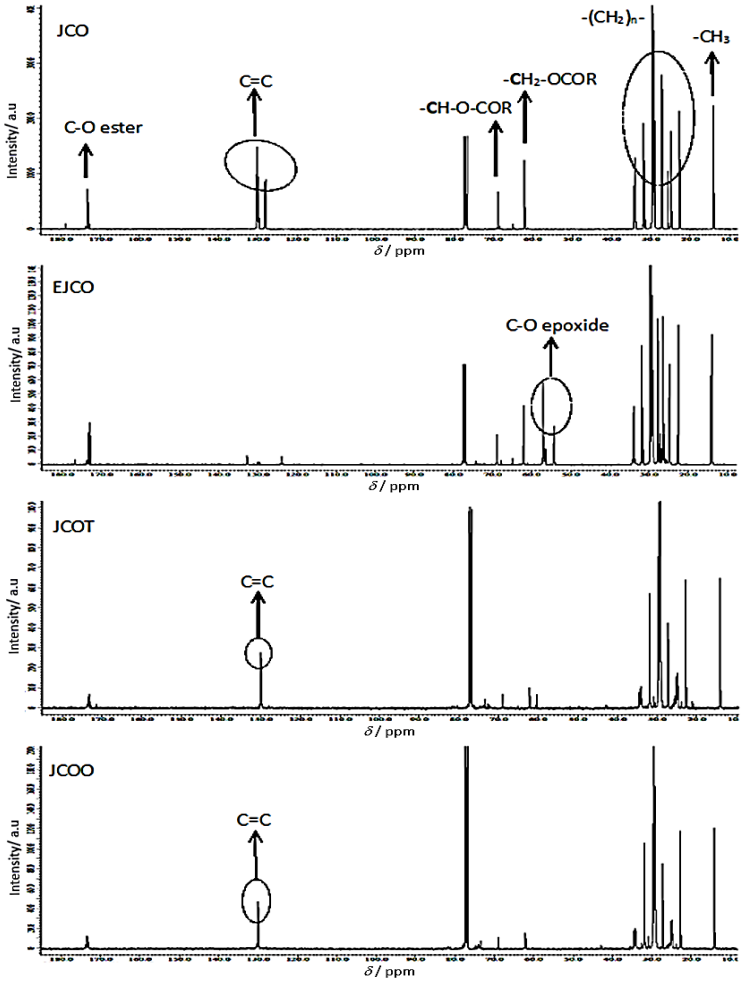

Figure 4. ^{13}C NMR spectra of JCO, EJCO, JCOT and JCOO

Table 2. ^{13}C NMR chemical shifts of JCO, EJCO, JCOT and JCOO

Compound	Chemical shift, ppm	Remarks
JCO	130.217, 130.026, 129.736, 128.115, 127.939	C=C
EJCO	57.159, 54.299, 54.146	C-O epoxide
JCOT	130.240, 130.057, 129.759	C=C
	73.590	C-O
JCOO	130.271, 130.065, 129.766	C=C

2. 4. Physicochemical properties

The obtained physicochemical properties are shown in Table 3. Increasing in the iodine values (IV) as the reaction product proceeds from JCO (113) to the final product of JCOO (660) proved that the esterification processes were successfully performed. Oxidative stability (OS) is determined by the onset temperature at which a sharp increase in the oxidation rate of the sample occurs. A high onset temperature indicates that the biolubricant has high OS [13]. Based on the DSC analysis, there is an improvement in OS for EJCO compared to JCO. This is due to the reduction in the content of double bonds that contributed to the reduction in the number of active sites for the oxidation process. However, JCOT and JCOO showed insignificant differences in OS due to the increasing carbon chain number and double bond content in the oil structure.

The ability of a substance to remain liquid at low temperatures is an important attribute for a number of industrial materials, such as biolubricants, surfactants and fuels [11]. The cold flow property of plant oils is extremely poor and this limits their use at low operating temperatures especially as automotive and industrial fluids. Plant oils tend to form

macro-crystalline structures at low temperatures through uniform self-stacking of the linear triacylglycerol molecules. Such macro-crystals restrict flow of the system due to the loss of kinetic energy of individual molecules during self-stacking [2, 3, 13]. JCOO has a lowest PP compared to the other products due to branching in the carbon chain and a bent structure. Self-stacking is thus restricted, and more hollow structure provide easier flowing which contributed to the lowest PP. In general, the presence of a branching group at the end of the molecule will disrupt the stacking process, create a steric barrier around the individual molecules and inhibits crystallization [11]. This will result in the formation of microcrystalline structures rather than macro-structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another resulting in better fluidity of the total matrix [2], resulting in a lower PP [11]. Moreover, disappearance of hydroxyl groups in JCOO esters means that hydrogen bonds do not exist in the molecule, which causes lower bonding of the molecules to each other and easier moving around [2].

Viscosity is one of the most important quality parameters for biolubricant oils. Efficiency of the biolubricant in reducing friction and wear is greatly influenced by its viscosity. Viscosity of oils decreases as temperature increases. It is desired to use a biolubricant with the lowest viscosity but still separating two moving surfaces. If the biolubricant is too viscous, it will require a large amount of energy to move, while if it is too thin, the surfaces will rub and friction will increase [2]. The VI value highlights how viscosity of a biolubricant changes with variations in temperature [2]. JCOT has a higher viscosity due to the presence of inter and intramolecular hydrogen bonding originating from hydroxyl groups as results of the ring opening reaction. Hydroxyl groups cause higher polarity that influences viscosity of the oil so that the more polar molecules, the higher the viscosity [13]. In general, hydroxyl groups will form bonds between molecules, which will cause that the lubricating oil becomes more viscous. After the final esterification process, viscosity of JCOO decreased due the disappearance of hydroxyl groups.

Table 3. Physicochemical properties of JCO, EJCO, JCOT and JCOO

Compound	JCO	EJCO	JCOT	JCOO	PAO6*
Iodine value, mg I_2 /100 g oil	113	5	330	660	-
Oxidative stability temperature, °C	174	179	169	170	201
Pour point, °C	-17	-9	-21	-29	-57
Flash point, °C	230	235	245	250	226
Kinematic viscosity at 40 °C, cSt	23.76	165.29	365.88	220.00	30.6
Kinematic viscosity at 100 °C, cSt	4.60	20.00	40.65	22.29	5.8
Viscosity index	111	124	127	135	132

*PAO6 = Polyalphaolefin lubricant

The FP value is often used as a descriptive characteristic of fuel oils as well as other oils such as biolubricants [2]. FP refers to both flammable and combustible oils [2]. Oils with a FP lower than 43 °C are flammable, while those with a FP above this temperature are combustible [2]. High FP is important to ensure that the biolubricant is not burned in the engine during its operation. A biolubricant with a low FP value is usually considered to be contaminated by volatile substances and usually requires precautions in handling [2]. JCOO shows the highest FP compared to the other products based on JCO due to the increase in the carbon number and consequently, increased molecular weight inducing a higher FP. In addition, JCOO also has a big branched carbon chain molecular structure, which requires more energy to burn and it will increase the FP.

For assessment purposes, the JCOO biolubricant produced in this work shows better lubrication properties as compared to those reported in literature for other biolubricants, especially regarding the oxidative stability (OS). In specific, JCOO shows high OS at 167 °C as well as values of PP (-29 °C), VI (135) and FP (250 °C). In comparison, a biolubricant in the same class, produced from a trimethylopropanol (TMP) ester of *J. curcas* oil showed significantly poorer low temperature properties with a high PP at -3°C and VI of 178 [26]. Other reports show moderate properties for similar biolubricants PP at –23 °C, FP (>130 °C) and VI (150) for 9(10)-hydroxy-10(9)-ester derivatives of methyl oleate [27]; PP at -3 °C, FP of 273 °C and VI at 140 for trimethylolpropane ester of *Jatropha curcas* oil [20]; and PP at −12°Cm FP of 178°C and VI at 204, for 9(12)-hydroxy-10(13)-oleoxy-12(9)-octadecanoic acid [29]. JCOO has also comparatively good lubrication properties as compared to a commercial PAO6 based lubricant (Table 3).

3. CONCLUSION

Chemical modification processes have been successfully performed significantly improving physicochemical and lubrication properties of the final product as compared to JCO itself. The epoxidation process has improved the OS and VI of the oil. The ring opening reaction has improved PP and FP values. Further esterification process with oleic acid has additionally improved the PP, FP and VI values of JCOO. The final product, JCOO has greater branching of ester functional groups with more bends and holes in its molecule structure. This makes the molecular arrangement less compact which improves the lubrication properties. Based on the obtained results, it is plausible that JCOO could be used as an industrial biolubricant with adequate lubrication properties.

Acknowledgements: Authors would like to acknowledge Universiti Kebangsaan Malaysia for the financial support through a research grant (DPP-2014-058, FRGS/2/2014/ ST01/UKM/01/2) as well as for the research facilities provided and to the Ministry of Education of Malaysia.

REFERENCES

[1] Campanella A, Rustoy E, Baldessari A, Baltanas M.A. Lubricants from chemically modified vegetable oils. *Bioresour Technol*. 2010; 101: 245–254.

[2] Jumat S, Nadia S, Yousif E. Chemically modified biolubricant basestocks from epoxidized oleic acid: Improved low temperature properties and oxidative stability. *J Saudi Chem Soc.* 2011; 15: 195–201.

[3] Jumat S, Nadia J. Oleic acid diesters: Synthesis, characterization and low temperature properties. *Eur J Sci Res.* 2009; 32; 216–222.

[4] Farhoosh R, Einafshar S, Sharayei P. The effect of commercial refining steps on the rancidity measures of soybean and canola oils. *Food Chem.* 2009; 115: 933–938.

[5] Erhan SZ, Asadauskas S. Lubricant basestocks from vegetable oils. *Ind Crops Prod.* 2000; 11: 277–282.

[6] Cerretani L, Bendini A, Rodriguez-Estrada MT, Vittadini E, Chiavaro E. Microwave heating of different commercial categories of olive oil: Part I. Effect on chemical oxidative stability indices and phenolic compounds. *Food Chem.* 2009; 115: 1381–1388.

[7] Moser BR, Sharma BK, Doll KM, Erhan SZ. Diesters from oleic acid:synthesis, low temperature properties, and oxidative stability. *J Am Oil Chem Soc.* 2007; 84: 675–680.

[8] Jumat S, Nadia S. Substituted esters of octadecanoic acid as potential biolubricants. *Eur J Sci Res.* 2009; 31: 273–279.

[9] Nirmal VP, Dineshbabu D. Performance and emission of *Pongamia Pinnata* oil as a lubricant in diesel engine. *Int J Innov Res Sci Eng Technol.* 2015; 4: 435–441.

[10] Wu X, Zhang X, Yang S, Chen H, Wang D. The Study of epoxidized rapeseed oil used as a potential biodegradable lubricant. *J Am Oil Chem Soc.* 2000; 77: 561–563.

[11] Jumat S, Nadia S. Modification of epoxidized ricinoleic acid for biolubricant base oil with improved flash and pour points. *Asian J Chem.* 2010; 22: 5468–5476.

[12] Lathi P, Mattiasson B. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. *Appl Catal B.* 2007; 69: 207-212.

[13] Ebtisam KH, Elmelawy MS, Salah AK, Elbasuny NM. Manufacturing of environment friendly biolubricants from vegetable oils. *Egypt. J. Pet*. 2017; 26: 53–59.

[14] Endalew AK, Kiros Y, Zanzi R. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Biomass Bioenergy*. 2011; 35: 3787–3809.

[15] Tahira F, Hussain ST, Ali SD, Iqbal Z, Ahmad W. Homogeneous catalysis of high free fatty acid of waste cooking oil to fatty acid methyl esters (biodiesel). *Int J Energy Power*. 2012; 1: 31–36.

[16] Hassani M, Amini G, Najafpour GD, Rabiee M. A two-step catalytic production of biodiesel from waste cooking oil. *Int J Eng*. 2013; 26: 563–570.

[17] Panadare DC, Rathod VK. Applications of waste cooking oil other than biodiesel: A review. *Iran J Chem Eng*. 2015; 12: 55–76.

[18] Arbain N, Jumat S. Synthesis and characterization of ester trimethylolpropane *Jatropha curcas* oil as biolubricant base stock. *J Sci Technol*. 2010; 2: 47–58.

[19] Muhammad FM, Gunam R, Tinia IMG, Azni I. Temperature dependence on the synthesis of Jatropha biolubricant. *IOP Conf Series: Mater Sci Eng*. 2011; 17: 1–11.

[20] Jumat S, Noor HA. The effects of various acid catalyst on the esterification of *Jatropha curcas* oil based trimethylolpropane ester as biolubricant base stock. *J Chem*. 2011; 8: 33–40.

[21] Sharma A, Adhvaryu A, Liu Z, Erhan SZ. Chemical modification of vegetable oils for lubricant applications. *J Am Oil Chem Soc.* 2006; 83: 129–136.

[22] Menkiti MC, Ocheje O, Agu CM. Production of environmentally adapted lubricant basestock from *Jatropha curcas* specie seed oil. Int J Ind Chem. 2017; 8: 133–144.

[23] Sharma A, Adhvaryu A, Liu Z, Erhan SZ. Chemical modification of vegetable oils for lubricant applications. *J Am Oil Chem Soc.* 2006; 83: 129–136.

[24] Moser BR, Erhan SZ. Preparation and evaluation of a series of α-hydroxy ethers from 9, 10-epoxystreates. *Eur J Lipid Sci Technol.* 2007; 109: 206–213.

[25] Wang R, Schuman TP. Vegetable oil-derived epoxy monomers and polymer blends: A comparative study with review. *eXPRESS Polym Lett.* 2013; 7:272–292.

[26] Yunus R, Razi AF, Iyuke TL, Idris A. Preparation and characterization of trimethylolpropane esters from palm kernel oil methyl esters. *J Oil Palm Res.* 2003; 15: 42–49.

[27] Sharma BK, Doll KM, Erhan SZ. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresour Technol.* 2008; 99:7333–7340.

[28] Akbar E, Yaakob Z, Kamarudin SK, Ismail M, Jumat S. Characteristic and composition of *Jatropha curcas* oil seed from Malaysia and its potential as biodiesel feedstock. *Eur J Sci Res*. 2009; 29: 396-403.

[29] Jumat S, Abdullah BM, Nadia S. Improvement of physicochemical characteristics of monoepoxide linoleic acid ring opening for biolubricant base oil. *J Biomed Biotechnol*. 2011; 2011: 1–8.

[30] Jumat S, Abdullah BM, Rahimi MY, Nadia S. Synthesis, reactivity and application studies for different biolubricants. *Chem Cen J*. 2014; 8: 1–11.

[31] AOCS, Official methods and recommended practices of the American Oil Chemists' Society, 4th ed., Champaign Illinois, USA, 1989.

[32] Nadia S, Jumat S, Jantan F. Synthesis and characterization of palm kernel oil based trimethylolpropane ester. *Asian J Chem*. 2013; 25: 9751–9754.

[33] Kishore, N.A. 2007. Guide to ASTM test methods for the analysis of petroleum products and lubricants, 2nd ed., ASTM International, West Conshohocken, PA, USA.

[34] Yunus R, Fakhru'l-Razi A, Ooi TL, Omar R, Idris A. Synthesis of palm oil based trimethylolpropane esters with improved pour points. *Ind Eng Chem Res*. 2005; 44: 8178–8183.

[35] Nadia S, Jumat J, Emad Y. The physicochemical and tribological properties of oleic acid based triester biolubricants. *Ind Crops Prod*. 2011; 34: 1089–1096.

[36] Abdo Ahmed W, Jumat S, Ambar YM. Lubricity characterizations of sebacic acid based ester. *Int J Adv Sci Eng Inf Technol.* 2014; 4: 1–6.

[37] Stachowiak GW, Batchelor AW. *Engineering Tribology*, 3th ed., USA, New York, Elsevier: Butterworth-Heinemann; 2005.

[38] Nor NM, Derawi D, Jumat S. Esterification and evaluation of palm oil as biolubricant base stock. *Malaysian J Chem*. 2019; 21: 28–35.

[39] Owuna FJ, Dabai MU, Sokoto MA, Dangoggo SM, Bagudo BU, Birnin-Yauri UA, Hassan LG, Sada I, Abubakar AL, Jibrin MS. Chemical modification of vegetable oils for the production of biolubricants using trimethylolpropane: A review. *Egypt J Pet*. 2020; 29: 75–82.

[40] Timothy YW, Sunday AL, Asipita SA, Moses AO. Nigeria Jatropha oil as suitable basestock for biolubricant production. *J Tribol*. 2019; 23: 97–112.

[41] Jagadeesh KM, Satish VK, Venkatesh K, Kathyayini N. Evironmentally friendly functional fluids from renewable and sustainable sources – A review. *Renew Sustain Energy Rev*. 2018; 18: 1787–1801.

[42] Jumat S, Abdullah BM, Yusop RM, Nadia S. Synthesis and optimization ring opening of monoepoxide linoleic acid using *p*-toluenesulfonic acid. *SpringerPlus*. 2013; 2: 1–14.

[43] Bilal S, Mohammed-Dabo I, Nuhu M, Kasim S, Almustapha I, Yamusa Y. Production of biolubricant from *Jatropha curcas* seed oil. *J Chem Eng Mater Sci*. 2013; 4: 72-79.

SAŽETAK

Hemijski modifikovano ulje biljke Jatrofa curcas za primenu kao biomazivo

Nurazira Mohd Nor[1], Nadia Salih[2] and Jumat Salimon[2]

[1]School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 72000 Kuala Pilah, Negeri Sembilan, Malaysia
[2]Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

(Naučni rad)

Ulje biljke *Jatropha curcas* jedan je od zanimljivih obnovljivih izvora za proizvodnju biomaziva. Međutim, direktna primena ovog ulja kao biomaziva je ograničena zbog njegove male oksidativne stabilnosti. Ovaj nedostatak može se prevazići modifikacijom strukture reakcijama epoksidacije, otvaranja prstena i esterifikacije. Epoksidacija ulja izvršena je *in situ* generisanom permravljom kiselinom, a otvaranje prstena reakcijom sa oleinskom kiselinom u prisustvu *p*-toluensulfonske kiseline . Potpuna esterifikacija oleinskom kiselinom izvršena je u prisustvu sumporne kiseline. Struktura modifikovanog ulja određena je merenjem sadržaja epoksi kiseonika, infracrvenom spektroskopijom sa Furijeovom transformacijom (engl. Fourier-transform infrared spectroscopy, FTIR) i nuklearno-magnetno-rezonantnom spektroskopijom (^{1}H NMR i ^{13}C NMR). Rezultati su pokazali da su oksidativna stabilnost, viskoznost, tačka paljenja i tačka tečenja krajnjeg proizvoda značajno poboljšani. Konkretno, postupci otvaranja i esterifikacije prstena koji dovode do grananja i savijanja u konačnoj molekulskoj strukturi ulja, doveli su do poboljšanja indeksa viskoznosti na vrednost od 135, tačke tečenja na -29 ° C i povećanja tačke paljenja na 250 ° C..

Ključne reči: epoksidacija; otvaranje prstena; esterifikacija; oleinska kiselina; ekološko biomazivo