

Optimization of High Yield Epoxidation of Malaysian Castor Bean Ricinoleic Acid with Performic Acid

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Abstract: Epoxidized castor oil (ECO) has shown high potential for industrial applications as value-added products such as polymer coating, plasticizer, and biolubricant. Epoxidized ricinoleic acid recovered from ECO has potential for industrial usage. In this work, epoxidized ricinoleic acid (ERA) was synthesized through in situ generated performic acid epoxidation of ricinoleic acid (RA). The epoxidation process was optimized by several reaction parameters, such as the molar ratio of formic acid to ethylenic unsaturation, the molar ratio of hydrogen peroxide to ethylenic unsaturation, and reaction temperature. The response reaction parameters of oxirane oxygen content (OOC) and iodine value (IV) were then evaluated. The results showed the optimal condition for the epoxidation of RA was obtained at 50 °C, the molar ratio of formic acid and hydrogen peroxide to ethylenic unsaturation of 1:8:1 for 4 h reaction time. A high yield of ERA of 86% with relative conversion into oxirane of 85.3% was achieved at the optimum condition. The optimum ERA showed a high OOC value of 4.00% and a low IV value of 2.24 mg/g. It is plausible that ERA can be used as an intermediate starting material to prepare value-added products such as biosurfactants, biopolymer additives, or biolubricants.

Keywords: in situ epoxidation; oxirane oxygen content; performic acid; ricinoleic acid

■ INTRODUCTION

Plant oils are extensively converted through mild chemical reactions or less extensive oleochemical processing to produce value-added products such as biosurfactants, biopolymer additives, biolubricants, and bio-resin [1-3]. These value-added products are produced based on the reactive headgroup and functional groups present in their fatty acids, and methyl esters of fatty alcohols as intermediates. These compounds are ready for chemical derivatization and modification to create products in industrial applications [4]. Therefore, naturally occurring specialized and functionalized fatty acid groups such as sulfonated fatty acids, oxygenated fatty acids, fatty acids with acetylenic bonds are in high demand due to their importance as industrial feedstocks. These fatty acid groups are also known as unusual fatty acid groups. Some known unusual fatty acid groups are epoxy, hydroxyl (mono- to poly-), keto, oxygenated,

sulfonated, and nitrogen functional groups. Due to the interesting chemical versatility of such functionalized fatty acids [5], researchers worldwide are studying new oilseed species that may be added as oleochemical industry raw materials. However, productions of these natural oils are limited to specific plant and animals species. Oilseed crops that supply hydroxylated fatty acids such as *Ricinus cummunis* (castor bean oil), *Lesquerella* spp. (lesquerella oil) [6], *Dimorphotheca* spp., *Vernonia* spp, *Euphorbia lagascae* (vernonia oil) [7] are of industrial interest. In fact, to date, the only commercially available naturally occurring functionalized fatty acid is ricinoleic acid, which is obtained from castor bean oil. Ricinoleic acid, *cis*-12-hydroxyoctadeca-9-enoic acid (9c, 12OH-18:1), contains monohydroxy monounsaturated fatty acid. The industrial usage of castor bean oil and its derivatives, such as epoxidized castor oil, has long been

reported as biolubricants, plasticizers, bioplastic, and bio coating [2,8-9].

Lesquerolic acid, 14-hydroxy-*cis*-11-eicosenoic (11c, 14OH-20:1), is another hydroxy fatty acid similar to castor oil's ricinoleic acid. Dehydration converts nondrying lesquerella oil into a drying oil with a drying velocity equivalent to that of commercial dehydrogenated castor oil. Vernonia oil has been proposed as precursors for adhesives, varnishes and paints, plasticizers, and industrial coatings [2]. Therefore, researchers began turning to oleochemistry and the potential use of uncommon functionalized fatty acids of vernolic acid (12,13-epoxyoctadecenoic acid or *cis*-12-epoxyoctadeca-*cis*-9-enoic acid or 12-epoxy-*cis*-9-octadecenoic acid) and dimorphecolic acid (9-hydroxyoctadecadienoic acid or 9-hydroxyoctadeca-10,12-dienoic acid) in a variety of high-value products [7,10]. Vernolic acid is a monounsaturated fatty acid that contains an epoxide in its fatty acyl chain. It is produced in abundance by the genera *Vernonia*, and *Euphorbia* spp., natural vernonia oil and is a potentially useful biofeedstock. However, in reality, the revolution of a new oilseed crop from trial plant species to an industrial commodity would be greatly challenging.

However, due to the limited availability of oxygenated, hydroxyl, epoxide functionalized fatty acids in the fatty acyl chain, reactions to modify unsaturated fatty acids become pertinent. For example, the feasibility of a mild chemical modification process such as an epoxidation reaction is worth to be utilized to produce a functionalized epoxide-fatty acid. Plant oils or fatty acids epoxidation can be economically accomplished by reacting the unsaturated double bonds of the fatty acid with a peracid reagent such as peracetic [11] or performic acid [1,12]. Currently, epoxides plant oils [13-16] or fatty acids are prepared on an industrial scale through *in situ* generated peracids [14]. The epoxidations of ricinoleic acid, for example, have been reported elsewhere [8-9,17-22]. Epoxidized ricinoleic acid received great attention due to the wide range of feasible further chemical modification reactions that can be involved. The epoxide oxirane ring's high reactivity makes it easily opened by moderate reaction conditions to produce a variety of value-added intermediates [23]. For instance, different

nucleophiles group attacks on epoxide rings could produce mono-alcohols, diols, alkoxyalcohols, hydroxyesters as intermediates for the production of value-added products such as biolubricants [8-9], bio plasticizer [24], biopolymer additives, or biosurfactants [25-26].

Our work has focused on the production of epoxidized ricinoleic acid (ERA), "vernolic acid-like acid," which contains an epoxy ring in combination with a hydroxy group, as shown in Fig. 1. This uniqueness makes ERA such an interesting building block for unique high-value-added products. The literature survey showed no reports about detailed optimization of the epoxidation of ricinoleic acid and its physicochemical properties. In this paper, the ERA was prepared through the epoxidation process of ricinoleic acid (RA) using *in situ* formed performic acid catalyst, and the epoxidation process was optimized. The parameters of the epoxidation process were optimized for the molar ratio of ricinoleic acid:formic acid:hydrogen peroxide, amount of catalyst, reaction temperature, and reaction time. In addition, the ERA product's reaction responses of oxirane oxygen content (OOC) and iodine value (IV) were evaluated.

■ EXPERIMENTAL SECTION

Materials

Castor bean seeds were collected from various places in Selangor and Kedah, Malaysia. Solvents of *n*-hexane, ethyl alcohol (95%), and chemicals of glacial acetic acid, sodium sulfate anhydrous, sodium chloride, potassium hydroxide, hydrochloric acid, formic acid (Fisher Scientific (USA)), aqueous hydrogen peroxide (30 wt.% Merck, Germany), and sodium hydrogen carbonate were purchased from System (UK). Wijs solution (QReC), hydrogen bromide, potassium iodide (Fluka), sodium thiosulphate, sodium chloride, and saturated sodium bicarbonate were purchased from Sigma Aldrich (UK), and crystal violet was from BDH Laboratory Supplies. All the chemicals used in this study were either analytical grade or high-performance liquid chromatography (HPLC) grade and were used without further purification.

Instrumentation

The molecule structure of epoxidized ricinoleic acid was analyzed by using Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy. FTIR spectra were recorded on a Perkin Elmer Infrared Spectrophotometer in 400–4000 cm^{-1} . In addition, the ^1H (16 scans) and ^{13}C -NMR (3000 scans) spectra were recorded on JEOL-ECP 400 spectrometer (400 MHz ^1H /100.61 MHz ^{13}C) using CDCl_3 as a solvent.

Procedure

Extraction of castor bean oil

Castor bean oil extraction was carried out using a Soxhlet extractor. About 100 g of dry ground seeds were first oven-dried at 105 $^\circ\text{C}$ for 1 h. Next, the oil was extracted by refluxing (55–60 $^\circ\text{C}$) the samples in *n*-hexane for 6 h in a Soxhlet extractor. The solvent was then evaporated using a rotary evaporator. The extracted castor bean oil was kept in an oven at 60 $^\circ\text{C}$ for 30 min before being accurately weighed. Finally, the extracted castor bean oil was kept in a closed container and stored in a desiccator.

Hydrolysis of castor bean oil

The castor bean oil (50 g) was hydrolyzed using 200 mL 1 M ethanolic KOH solution (95% v/v) in a reflux apparatus for 2 h. The hydrolysis product and fatty acid mixture were then neutralized with 200 mL 1 M HCl and washed with 200 mL distilled water before extracting with 100 mL ethyl acetate. The organic layer was dried with anhydrous sodium sulfate overnight. Finally, the solvent was evaporated to yield a light-yellow liquid containing a mixture of fatty acids mixture.

Oxirane oxygen content (OOC%) determination

Around 0.3 g of sample was weighed in a 50 mL Erlenmeyer flask and dissolved in 10 mL benzene. Five drops of 0.1 g of the crystal violet indicator in 100 mL glacial acetic acid were gradually added into the sample solution [27]. A rubber stopper was placed to cover the titration flask and magnetically stirred at room temperature for 5 min. The sample solution was gradually stirred and titrated rapidly with 0.1 M HBr solution (prepared in acetic acid) to a bluish-green endpoint that persisted for 30 s. The experiments were done in triplicate.

The Equations 1, 2 and 3 were used to calculate the experimental oxirane oxygen content (OOC_{exp}) value, theoretical OOC (OOC_{theo}), and the relative percentage of conversion to oxirane (RCO), respectively.

$$\text{OOC}_{\text{exp}} = \frac{V \times M \times 1.60}{W} \quad (1)$$

where: V = volume (mL) of the HBr titrant solution, M = molarity of the titrant, W = weight (g) of the sample, 1.6 = Atomic weight of oxygen divided by ten.

$$\text{OOC}_{\text{theo}} = \frac{IV_o / 2A_i}{100 + (IV_o / 2A_i)} A_o \times 100 \quad (2)$$

where: IV_o = initial iodine value, A_i = atomic weight of iodine (g mol^{-1}), A_o = atomic weight of oxygen (g mol^{-1}).

$$\text{RCO} = \frac{\text{OOC}_{\text{exp}}}{\text{OOC}_{\text{theo}}} \times 100 \quad (3)$$

where: OOC_{exp} = experimental OOC, OOC_{theo} = theoretical OOC (max).

Iodine value (IV) determination

The sample's iodine value (IV) was calculated according to the AOCS Official Method Cd 1-25. About 0.4 g of sample was placed in a 500 mL flask. The sample was dissolved in an aliquot of 15 mL carbon tetrachloride (CCl_4). A Wijs solution (25 mL) was added to the flask and covered with a rubber cork stopper. The mixture in the flask was vigorously shaken and then left in the dark for 60 min. After 1 h incubation, 150 mL of distilled water and 20 mL of 10% KI solution were added to the mixture. The titrant 0.1 N sodium thiosulphate solution was used to titrate the mixture until the liquid turned yellow and reached the endpoint. Then, 1 mL of 1% starch indicator solution was added. The titration was continued while the solution mixture was vigorously shaken until the blue color completely vanished at the titration endpoint. According to Yildiz et al. [28], the experiments were done in triplicate. The blank solution was treated under the same conditions. The IV value was calculated using Eq. (4):

$$IV = \frac{12.69 \times N (V_b - V_s)}{W} \quad (4)$$

where: N = exact normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution (eq/L), V_b = volume (mL) of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for blank titration, V_s = volume (mL) of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for sample titration, W = weight (gram) of sample, 12.69 =

equivalent thiosulphate weight to gram iodine (relative molecular mass of iodine = 126.9).

Synthesis of epoxidized ricinoleic acid

The epoxidation reaction of ricinoleic acid (RA) was carried out according to Salimon et al. [9]. The optimization of the epoxidation process was set at a molar ratio of RA:HCOOH:H₂O₂ (1:1:X), reaction temperature range of 30–70 °C, and reaction time range of 1–5 h. At first, variable X was set to 1–10 mol of H₂O₂. After variable X was obtained, the following optimization process was then set at a molar ratio of RA:HCOOH:H₂O₂ (1:Y:X). Next, variable Y was set at 0.4–1.2 mol of HCOOH. The important reaction response parameters involved to produce a high yield with significant reaction responses of high OOC and low IV values were examined. The epoxidation process was carried out in a round bottom flask equipped with a reflux condenser, thermometer, and magnetic stirrer. At selected parameters for the optimization, a solution of 1-mol hydrogen peroxide solution was slowly added to a stirred mixture solution of ricinoleic acid:formic acid in 1:1 mol ratio at 4 °C (ice bath). Then the reaction proceeded at a selected temperature (30–70 °C) with vigorous stirring (900 rpm) until a powdery solid formed in the reaction vessel at the selected reaction time (1–5 h). After the reaction complete, the catalyst and remaining unreacted RA were neutralized by adding saturated sodium chloride, saturated sodium bicarbonate, and 1 M NaOH solutions. The solid was collected via vacuum filtration, washed with H₂O (chilled, 3×10 mL), and dried for 12 h under high vacuum to provide epoxidized ricinoleic acid (ERA) as a white, powdery solid. Every experiment was repeated in triplicate. The same procedure was repeated for different optimization reaction parameters, and the results were presented as mean ± standard deviation.

RESULTS AND DISCUSSION

Synthesis of Epoxidized Ricinoleic Acid

In this study, the results showed that Malaysia's castor bean seeds contain a relatively high percentage, 45% of oil content, well in agreement with the previous report. The hydrolysis of extracted castor oil produced a dominant ricinoleic acid (RA) content at 86% and was

used as a representative of the mixture of castor oil fatty acids. RA was converted into epoxidized ricinoleic acid (ERA) through the *in situ* generated performic acid as the epoxidation catalyst. Hydrogen peroxide solution was slowly added to a reaction solution containing RA and formic acid to avoid the sudden exothermic conditions where it could lead to the reopening of the epoxide ring at a high temperature of the acidic reaction medium. Fig. 1 shows the epoxidation reaction of RA producing ERA.

The Optimization of the Epoxidation Process

The optimization process for the epoxidation of RA was performed to produce the optimum values or higher yields and OOC reaction responses. The interaction between all variable parameters and criteria chosen for all the reaction responses affected the optimum reaction conditions. The effect of the reaction temperature, reaction time, substrate molar ratio (molar ratio of hydrogen peroxide and formic acid for the double bond in RA), and the amount of *in situ* catalysts (performic acid) were selected as parameters to determine the most optimum reaction condition. The optimization process was first set at a molar ratio of RA:HCOOH:H₂O₂ (1:1:X), the reaction temperature in the range of 30–70 °C, and the reaction time range of 1–5 h. The important reaction response parameters involved to produce high reaction yield with significant-high reaction responses of OOC and significant low IV values were examined.

The Effect of Hydrogen Peroxide Molar Ratio

The optimization process was first set at the molar

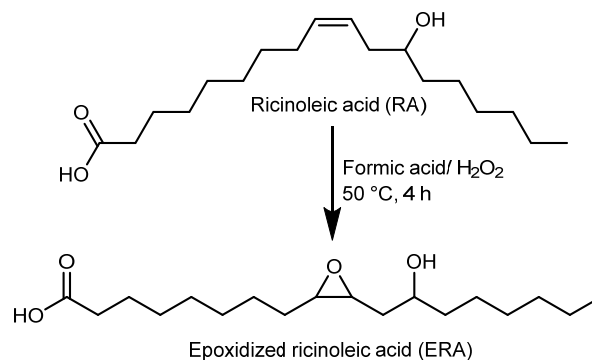


Fig 1. The chemical reaction synthesis of ERA

ratio for RA: HCOOH:H₂O₂ at 1:1:X and fixed reaction temperature of 40 °C and reaction time of 5 h. Variable X was set from 1 to 10 mol of H₂O₂. Hydrogen peroxide acts as an oxygen donor in the epoxidation process. The influence of the H₂O₂ amount at selected reaction conditions on the ERA yield, IV, and OOC values is shown in Fig. 2. The results have shown that increasing the moles of H₂O₂ increased the ERA yield and OOC. Higher values of yield and OOC were obtained at 8 mol of H₂O₂. Increasing H₂O₂ moles up to 8 increased the OOC value to 4% with 85.3% RCO and 85% ERA yield due to effective performic acid catalyst formation. However, a high amount of H₂O₂ must be avoided because it raised the additional agitation problem and decreased the mass transfer rate, thereby decreasing the OOC [18]. A high concentration of H₂O₂ also causes the epoxy-functional group to become unstable [29]. Higher H₂O₂ causes the stability of the oxirane ring to reduce and leads to an accelerated rate of oxirane ring decomposition or degradation [18], which is in agreement with the report for the stability of epoxide sunflower and soybean oil degraded at 30 wt.% H₂O₂ [30]. Others reported that the cleavage of oxirane rings of epoxide oleic acid-based palm oil was affected the most by hydrogen peroxide, followed by formic acid, which leads to the formation of diol and α -glycol as side products [31].

The Effect of the Formic Acid Molar Ratio

Formic acid, HCOOH, can act as an oxygen carrier and be regenerated once the epoxidation reaction occurs [32]. HCOOH also takes part in the overall reaction as a catalyst (performic acid) in the formation of the oxirane ring. At the same time in an acidic medium, HCOOH serves as a reactant in the hydrolysis or degradation of the oxirane ring and should be avoided. The next optimization process was set at the molar ratio for RA:HCOOH:H₂O₂ at 1:X:8, fixed reaction temperature of 40 °C and reaction time of 5 h. Variable X was set at 0.4 to 1.2 mol of HCOOH. The results showed that an increasing amount of HCOOH increased the ERA yield and OOC value, as reflected by its RCO percentage (Fig. 3). High yield percentage and OOC were observed at high HCOOH amount range of 0.8–1.2 mol. Increasing the

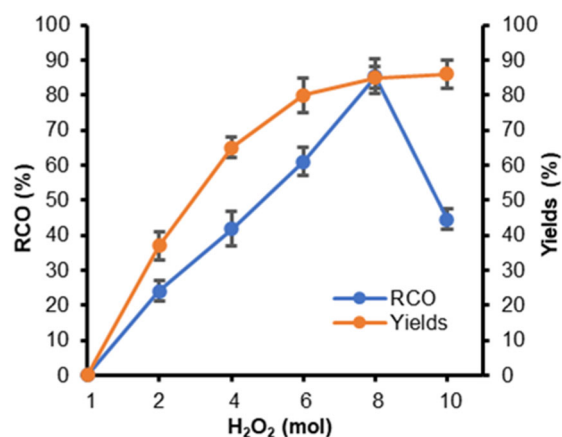


Fig 2. Effect of H₂O₂ molar ratio on RCO and yields

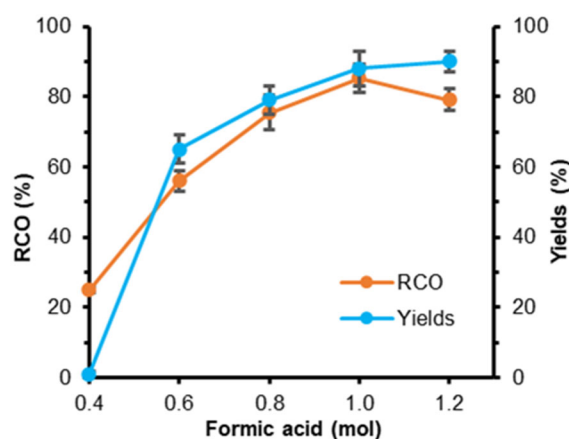


Fig 3. Effect of formic acid molar ratio on RCO and yields

mole of HCOOH up to 1.0 mol had increased OOC value to 4.0%. However, further increment of HCOOH amount led to a decline in the OOC. When the HCOOH mole was higher than 1.0 there was a decrease in ERA yield (90%) and OOC (reduced to 3.71%). The maximum OOC value was attained using the optimum level of formic acid where it acts as an oxygen carrier for the formation of the required peracid catalyst and the epoxy ring hydrolysis are equilibrated [33]. High concentrations of HCOOH may cause the epoxy ring to degrade, thus this condition needs to be avoided [29]. Increasing the HCOOH concentration had a detrimental effect on the epoxide ring due to the epoxide ring being unstable in an acidic medium and hence easier to be degraded [30]. Therefore, the epoxide ring's hydrolysis was promoted and reduced the final OOC value [31], which agrees with the report that stated that

the epoxide ring degraded faster at the molar ratio of epoxidized oleic acid-based palm oil to HCOOH of 1:1 [31].

The Effect of Reaction Temperature

The next optimization process was set at a molar ratio of RA:HCOOH:H₂O₂ at 1:1:8, a reaction time of 5 h, and a reaction temperature in the range of 30–70 °C. The results showed that high values of yield and OOC were achieved at reaction temperatures between 40–60 °C (Fig. 4). Increasing the reaction temperature increased the ERA OOC value (shown by its RCO) as the peroxy acid catalyst (performic acid) increased. However, further increment of reaction temperature led to a decline in OOC value. Reaction temperatures of higher than 50 °C decreased ERA yields to less than 78.3% and OOC down to 1.18%. The higher concentration of performic acid must be controlled to avoid extreme exothermic epoxidation conditions, leading to low oxirane ring stability [30].

The Effect of Reaction Time

The final optimization process was set at a molar ratio of RA: HCOOH: H₂O₂ (1:1:8), reaction temperature of 50 °C, and reaction time range of 1–5 h. As mentioned earlier, a high concentration of performic acid (as the reaction time is prolonged) must be avoided due to the exothermic epoxidation process, which leads to the low stability of the oxirane ring formed [29]. The reaction time increment up to 4 h increased the ERA yield up to 91.1% and RCO to 85.3 % (Fig. 5). Further increase in reaction time caused a decrease in the epoxide yield. Due to the degradation of the oxirane ring, more by-products are formed, and the undesirable oxirane ring-opening reaction occurs [34]. The results have shown that the optimal RA epoxidation reaction conditions were achieved at a molar ratio of RA:HCOOH:H₂O₂ at 1:1:8, reaction temperature of 50 °C, and reaction time of 4 h.

The final triplicate confirmation experiments have shown that at the optimal RA epoxidation reaction condition, the white powdery solid of ERA was produced at 86% yield with an OOC value of 4.0 (85.3% RCO) and IV value of 2.33 mg/g. In this study, OOC for the ERA was 4.69%, equivalent to 0.29 mol of oxygen/100 g of

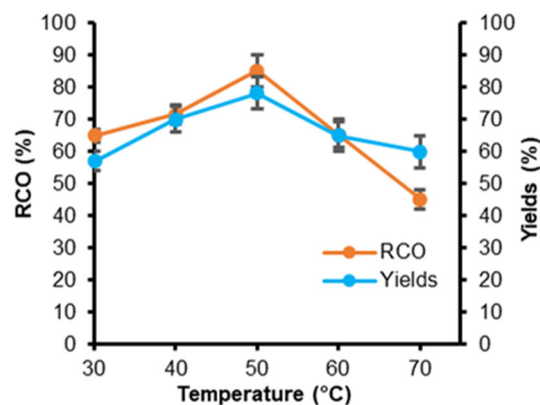


Fig 4. Effect of reaction temperature on RCO and yields

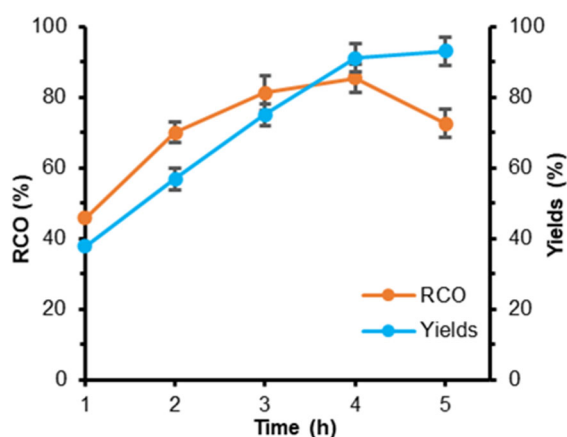


Fig 5. Effect of reaction time on RCO and yields

epoxidized RA or ERA. This value is lower than 0.34 mol of oxygen/100 g of epoxidized sunflower oil [30]. The theoretical IV value of ERA is 77.63 mg/g RA. Therefore, the theoretical relative conversion to oxirane ring oxygen (RCO_{the}) is 97%. Thus, it indicates that about 11.7% of the oxirane ring in ERA had been degraded or hydrolyzed during the epoxidation process at the optimal condition. Nevertheless, this is an acceptable value in an adequate reaction control condition because the epoxidation process requires an acidic medium.

Product Characterization

FTIR peaks of RA indicate an unsaturation functional group at 3010 cm⁻¹ (Csp²-H) 3010 cm⁻¹ (C=C). After the epoxidation of RA, the unsaturation peak disappeared, and an additional new peak appeared in the 823–843 cm⁻¹ range. The appearance of an epoxy peak at 825 cm⁻¹ provided evidence that epoxidation

reaction took place using *in situ* performic acids as a catalyst. The change of functionality in this range indicates that all the unsaturation content was transformed into epoxide products (Fig. 6). Salimon et al. [9] described that the characteristic signals in the FTIR spectrum of RA at 823–843 cm^{-1} represent the tertiary carbons of the oxirane ring. The complete disappearance of C=C bonds in the ERA epoxide spectra further indicates the almost complete conversion of double bonds to oxirane (i.e., 85.3%). In this study, FTIR spectra exhibited the –OH absorption peak at approximately 3400–3500 cm^{-1} , representing the hydroxyl groups belonging to the RA.

The epoxidized compound was synthesized to produce an intermediate compound such as ERA to produce a value-added product such as bio lubricant base stock. The $^1\text{H-NMR}$ spectra of RA and its epoxide, ERA, are shown in Fig. 7. During the epoxidation of RA, the unsaturation group was converted into an oxirane ring. The chemical shift, δ of the unsaturation in RA, was shown at 5.3 to 5.6 ppm (Fig. 7). The epoxidized product, ERA, was confirmed by the disappearance of the double bonds of the unsaturation and the appearance of a new chemical shift of the epoxy group (oxirane ring) at δ 1.45 and 2.47 ppm (Fig. 7). Similar observations were observed by Salimon et al. [9] during their study on ricinoleic acid epoxidation and Borugadda and Goud [18] for the

epoxidation of castor oil.

Furthermore, the presence of unsaturated acyl carbon groups in RA was determined by identifying the alkene group (C=C). The alkene group (C=C) in RA was detected at the chemical shift of 132.30 ppm [35] as shown in Fig. 8. The disappearance of this unsaturation peak of RA was replaced by the appearance of a new carbon epoxy group of ERA that proved the success of the epoxidation process. Significant signals of new chemical shifts were observed at 56.82 and 56.86 ppm for a doublet corresponding to the oxirane ring's carbons and a chemical shift at 32.84 ppm for carbon adjacent to the oxirane ring (Fig. 8). The same observation was reported by Salimon et al. [9].

NMR spectra multiplet reports for RA and ERA are as follows:

RA - $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 0.76–0.86 (m, 3 H), 1.30–1.32 (d, $J = 13.73$ Hz, 22H), 1.40–1.43 (m, 2H), 1.59–1.60 (m, 2H), 2.00–2.02 (m, 2H), 2.22–2.26 (m, 2H), 2.29–2.30 (m, 2H), 3.62–4.05 (s, 1H), 5.40–5.50 (m, 1H), 5.51–5.55 (m, 1H), 6.50–6.52 (br. s., 1H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ ppm 14.12 (s, 1C), 22.71 (s, 1C), 24.71 (s, 1C), 25.19 (s, 1C), 27.24 (s, 1C), 29.15 (s, 1C), 29.20 (s, 1C), 29.37 (s, 1C), 29.57 (s, 1C), 29.73 (s, 1C), 31.40 (s, 1C), 34.17 (s, 1C), 35.50 (s, 1C), 37.12 (s, 1C), 71.30 (s, 1C), 123.21 (s, 1C), 132.30 (s, 1C), 179.50 (s, 1C).

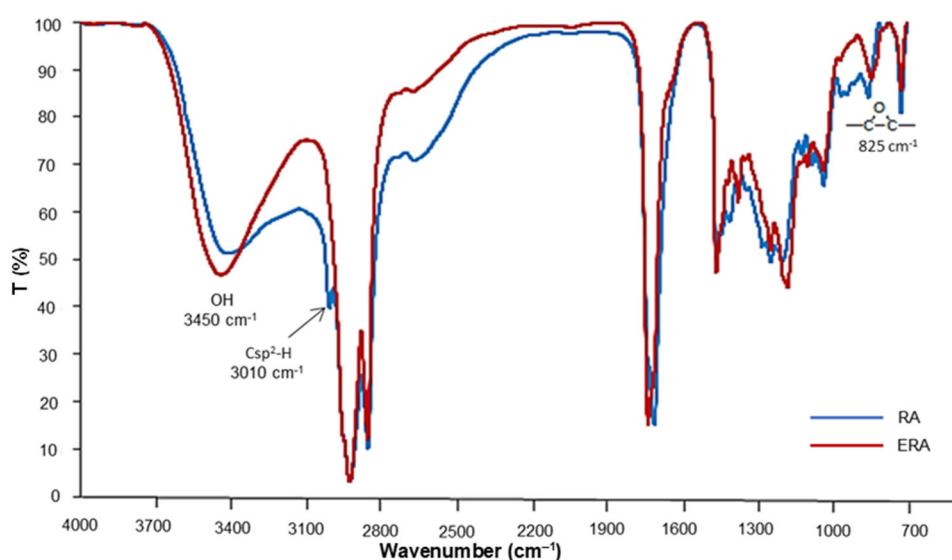


Fig 6. FTIR spectra of RA and ERA

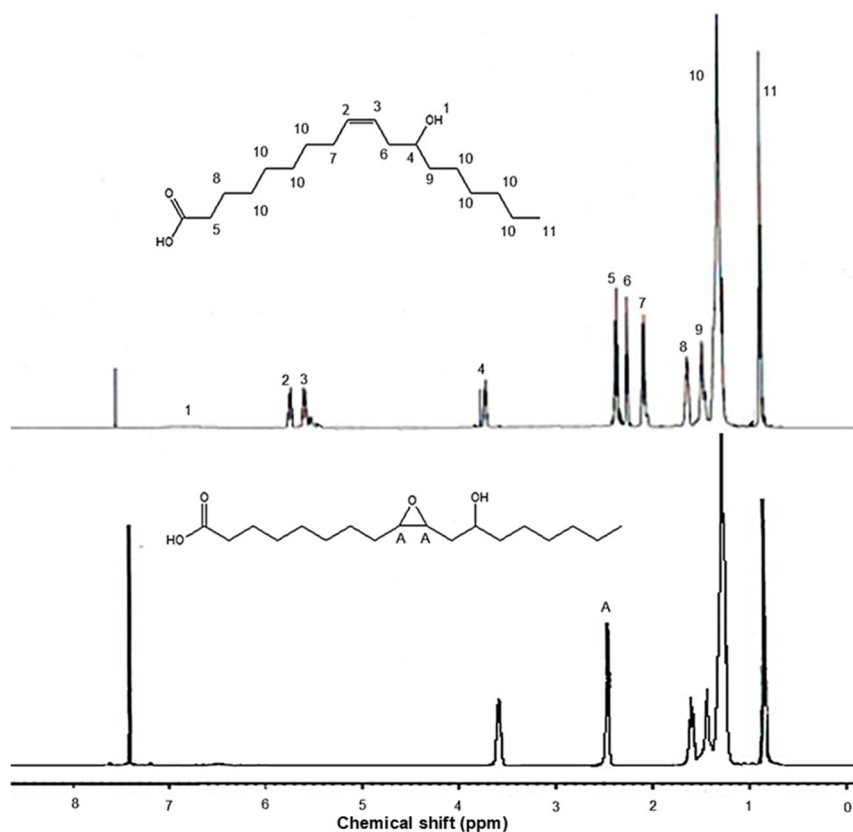
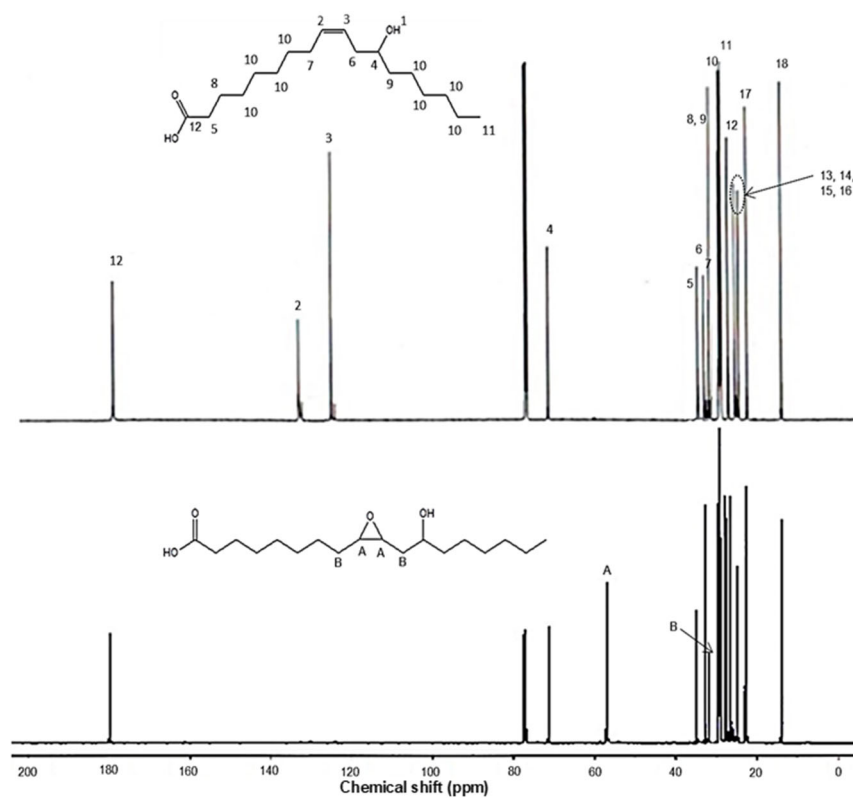
Fig 7. ¹H-NMR spectrum of RA and ERAFig 8. ¹³C-NMR spectrum of RA and ERA

Table 1. Physicochemical properties of epoxidized plants oil and epoxidized ricinoleic acid

Property	ESO ^a	ECO ^b	ERA
Refractive index (@ 25 °C)	1.470	1.412	1.274
Epoxy/Oxirane Oxygen Content value, (%)	6.6 min	4.84	4.0
Acid value, (KOH mg/g)	0.5 max	1.32	128
Iodine value, (g I ₂ /100 g)	2.8 max	6.34	2.24
Flash point, (°C)	280 min	285	250
Pour point (°C)	10	-11	30

Note: ESO = Epoxidized soybean oil [34], ECO = Epoxidized castor bean oil [22], ERA = Epoxidized ricinoleic acid (this study)

ERA - ¹H-NMR (400 MHz, CDCl₃): δ ppm 0.76–0.86 (m, 3H), 1.30–1.32 (d, *J* = 13.73 Hz, 22H), 1.40–1.43 (m, 2H), 1.45–1.47 (m, 2H), 1.59–1.60 (d, *J* = 7.48 Hz, 2H), 2.29–2.30 (m, 2H), 2.47–2.49 (m, 2H), 3.62–4.05 (s, 1H), 6.50–6.52 (br. s., 1H); ¹³C-NMR (101 MHz, CDCl₃): δ ppm 14.12 (s, 1C), 22.71 (s, 1C), 29.15 (s, 1C), 29.20 (s, 1C), 29.37 (s, 1C), 31.11 (s, 1C), 31.11 (s, 1C), 31.11 (s, 1C), 31.11 (s, 1C), 31.11 (s, 1C), 31.40 (s, 1C), 31.41 (s, 1C), 32.84 (s, 1C), 34.17 (s, 1C), 56.82 (s, 1C), 56.90 (s, 1C), 71.50 (s, 1C), 179.6 (s, 1C).

Physicochemical Properties

In this study, the resulting ERA showed relatively high epoxy value or OOC content compared to epoxidized castor bean oil (ECO) and commercial epoxidized soya bean oil (ESO). Table 1 shows the comparative physicochemical properties of ESO, ECO, and ERA. Most of the epoxidized plant oils showed relatively high OOC and low IV values. ESO has been commercialized and shown to enhance soft PVC's softness and shine due to it being a good plasticizer and stabilizer for PVC. The enhancement of the modified PVC includes good sunlight-resistance, heat-resistance, and low volatility. Soy-based polyurethane (PU) made from soybean oil through preliminary epoxidation, followed by methanolysis of the ESO resulting in soy-methanol polyol with suitable resultant soy-methanol polyol diisocyanates has been reported [36]. Most epoxidized plant oils are used as components of polyurethane compositions [35], plasticizers, and stabilizers of polymers [36]. The same range of industrial application has been shown by ECO [4,18,21-22]. This study showed that the obtained ERA had similar

properties to ESO and ECO. This indicates that it is plausible for ERA to be used in the same industrial application as ESO and ECO, particularly for biolubricants application [8-9].

CONCLUSION

The epoxidation process of RA was successfully optimized. The optimum reaction conditions were obtained at a molar ratio of RA:HCOOH:H₂O₂ of 1:1:8, reaction temperature of 50 °C, and reaction time of 4 h. At this optimum condition, the yields of RCO and ERA were 85.3% and 86%, respectively. The resulting ERA showed a high OOC value of 4.0 % and a low IV value of 2.24 mg/g. The results showed that all reaction variables significantly affected the reaction responses and strong interactions between reaction variables on the epoxidation process. The optimized conditions had successfully produced a high epoxide product (ERA) with high OOC value and are plausible to be used as an intermediate compound for further production of high-end and value-added products such as biolubricants.

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