

Research Article

Optimization for Epoxidation of Malaysian *Jatropha curcas* Oil Based Trimethylolpropane Ester Biolubricant

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Abstract

Epoxidized *Jatropha curcas*-based trimethylolpropane triester (ETMPJO) was prepared by *in-situ* epoxidation reaction using trimethylolpropane ester (TMPJO) and catalyzed by hydrogen peroxide (H_2O_2) in the presence of formic acid. The epoxidation process was optimized through variable parameters, such as hydrogen peroxide to tmpjo molar ratio, formic acid to TMPJO molar ratio, temperature, and time of the epoxidation reaction. The results showed the epoxidation optimal condition was achieved at the molar ratio of TMPJO to H_2O_2 and formic acid of 1: 2.0 and 1: 2.5, the temperature of 50 °C for 2 h, respectively. The obtained ETMPJO was characterized using Fourier transformation infrared (FTIR), nuclear magnetic resonance (NMR) spectroscopies, and gas chromatography analysis. The FTIR spectrum of ETMPJO showed the appearance of peaks at 825 and 908 cm^{-1} for the epoxy functional group. 1H NMR spectrum showed a chemical shift at 2.88 ppm of the epoxide group protons. ^{13}C NMR spectrum showed the chemical signal of carbon epoxide group at 54–57 ppm. At the optimal condition, the resultant ETMPJO obtained 91% yield with a comparatively high relative conversion oxirane (RCO) of 87%. With high oxygen oxirane content (OOC) of 4.38, ETMPJO owns a good characteristic for an intermediate compound for possible further conversion to produce high-end products. Moreover, its physiochemical and lubrication characteristics indicated that ETMPJO could be used as biolubricants for industrial applications.

Keywords: *In-situ* epoxidation, *Jatropha curcas*-based trimethylolpropane triester, Epoxidized trimethylolpropane triester

1 Introduction

Researchers continuously making their effort to develop new green biolubricants that are less sensitive to temperature change and comparatively oxidative stable. In addition to its property as raw material that are reproducible and biodegradable, green biolubricants should poses as an effective protective fluid at low temperatures, less volatility at high temperatures, and molecularly stable at any machine operating conditions. Plant oil has been known as natural biolubricant for mild

machine operating conditions. It could be used as a hydraulic fluid, engine oil, or transmission oil. Plant oil-based lubricants are biodegradable [1], [2]. This feature provides advantages to plant-based biolubricants due to its comparatively low-cost raw material than conventional mineral-based lubricants.

Since plant oil has low hydrolytic and thermo-oxidative stability, it is not suitable for heavy and extreme industrial applications. This is due to the β -H atom presence on the middle carbon of the glycerol backbone in the triacylglycerol (TAG) structure. This

leads plant oil esters more susceptible to oxidation and thermally unstable through the elimination of β -H, leading to the subsequent degradation process [3], [4]. The presence of a high unsaturation degree in plant oil (high composition of unsaturated ($-C=C-$) fatty acids) contributes another unfavorable direct usage direct biolubricant usage. These drawbacks can be mitigated via suitable modifications processes to the plant oil structure. Some green mild chemical mitigation approaches have been introduced to make plant oil lubrication properties more desirable. For example, the plant oil was chemically modified by replacing the glycerol backbone with polyhydric alcohol such as ethylene glycol (EG), trimethylolpropane (TMP), di-trimethylolpropane (di-TMP), pentaerythritol (PE), and di-pentaerythritol (di-PE) [4]. The unsaturation functional group in plant oil was eliminated through the epoxidation process to produce an epoxide functional group either to improve the oxidation stability or for further chemically modification process [4], [5].

Chemical modification has been proved as a promising method to improve plant oil-based biolubricants. Plant oil-based biolubricants have been reported elsewhere. Biolubricants-based on soybean [6], rapeseed [7], sunflower [8], palm oil [9], palm kernel oil [10], castor bean [7]. *Jatropha curcas* (*J. curcas*) oil [11], [12] has been reported to have good lubrication properties after being remediated with some chemical modifications processes. Biolubricants-based on *J. curcas* oil has shown good/excellent lubricant properties after reacting with TMP to produce TMP tri-ester [13]. The pour point of the product was as low as $-30\text{ }^{\circ}\text{C}$, the flashpoint was $>300\text{ }^{\circ}\text{C}$, and the kinematic viscosity at $40\text{ }^{\circ}\text{C}$ was 79 cP. However, its oxidative stability was low due to the high unsaturation composition. *J. curcas* oil composes about 20% total saturated fatty acids, mainly palmitic acid (16 : 0) with 10.5–14.1%, and stearic acid (18 : 0) with 2.3–6.7%. Whereas total unsaturated fatty acids were 80% consist of oleic acid (18 : 1) of 41.5–48.8%, and linoleic acid (18 : 2) of 34.6–47.4 % [14]–[18]. To improve the oxidative stability of TMP ester, further chemical modifications such as the epoxidation of the unsaturated fatty acid composition are of researches interest [19], [20].

The epoxidation process is the industry's most widely used chemical modification process towards highly unsaturated plant oils such as soybean oil, rapeseed, sunflower, etc. To increase their targeted

industrial use, the unsaturated oil will be converted to epoxidized oil either by pre- or *in-situ*-formed organic peracids [21]. To enhance the oxidative stability of plant oils, less oxidative stability at a double bond functional group will be replaced by a stable epoxy group [14]. Epoxidized oils have a wide range of commercial and industrial uses due to the high strain energy of the three-membered oxirane rings of the epoxy-functional group. Therefore, it offers a wide spectrum of varied chemicals reactivity for the next level of modification processes [14], [22]. Due to the high reactivity, epoxidized oils have been used as renewable raw materials to produce many industrial intermediate products such as alcohols, glycols, alkoxyalcohol, hydroxy esters, hydroxyalkyl amides, mercaptoalcohols, hydroxy nitriles, alkanol amines, and carbonyl compounds [23]–[25]. These important intermediates compounds have an important use in the production of industrial lubricants [26], [27], detergents, stabilizers, and plasticizers in polyvinylchloride (PVC) [28], coating materials [29], [30] etc. The epoxidation of plant oils, such as mahua oil [31], *J. curcas* oil [30]–[32], soybean oil [33]–[35], rubber seed oil [36], canola oil [37], rapeseed oil [38], jojoba oil and castor oil [39] have been investigated. However, the epoxidation of plant oil-based TMP ester has been less reported elsewhere. In this study, a polyol ester (TMP triester) derived from *J. curcas* oil via the epoxidation and optimized. The effect of several reaction parameters, such as reactant's molar ratios, reaction temperature, and reaction time on the epoxidation process was investigated. The important response variable parameter such as epoxidized TMP tri-esters oxirane oxygen content (OOC) and iodine values was examined and evaluated.

2 Materials and Methods

2.1 Materials

Malaysian *J. curcas* seeds were obtained from UKM, green biolubricant experimental plots, located at Selangor, Malaysia. *Jatropha curcas* oil-based TMP triester (TMPJO) was prepared according to Nor and Salimon [9] and used for the starting material. Formic acid (88%) was obtained from Fisher Scientific (USA) and hydrogen peroxide 30% from Merck, Germany. Trimethylolpropane, carbon tetrachloride, and

potassium iodide were purchased from Fluka. Sodium bicarbonate and sodium chloride were obtained from System. All the chemicals used in this study were either analytical grade or High Performance Liquid Chromatography (HPLC) grade and were used without further purification.

2.2 Epoxidation reaction of TMPJO

The epoxidation reaction of TMPJO was carried out according to Milchert and Smagowicz [40] with slight modification. The reaction was carried out in the three-neck round bottom flask equipped with a thermometer, a magnetic stirrer, and a reflux condenser. During the epoxidation reaction, performic acid was in situ formed by the reaction between formic acid (HCOOH) and hydrogen peroxide (H₂O₂) in the reaction mixture. About 50 g of TMPJO was placed into the reaction vessel. A required amount of formic acid and H₂O₂, calculated for a 1:2.5 mole ratio, was then added. Under continuous stirring, 30% aqueous hydrogen peroxide (H₂O₂) was added drop-by-drop. The reaction temperature was regulated by a circulating water bath for heating and cooling (5–90 °C). The reaction mixture was kept under continuous stirring to avoid zones of high concentration of peroxide that could lead to extremely high temperatures. After reaction completion, the mixture was transferred to a separating funnel. The organic layer was thoroughly washed with distilled water, 5% sodium carbonate and 5% sodium chloride solutions to neutralize the residual acid and remove the resulting salt from the reaction mixture. The final product, epoxidized TMPJO (ETMPJO), was then dried at 70 °C under reduced pressure of 20 mbar. The optimal parameters to obtain ETMPJO with OOC value nearest to the theoretical value and the stability of the OOC ring was maintained with a low iodine value (IV) will be established through the optimization process.

2.3 Determination of oxygen oxirane content (OOC)

A 0.3 g of the sample was weighed in a 50 mL Erlenmeyer flask and dissolved in 10 mL benzene. 0.1 g of the crystal violet indicator in 100 mL glacial acetic acid (5 drops total) were gradually added into the sample solution [40]. A rubber stopper was placed to cover the titration flask and magnetically stirred. While the sample solution was stirred, it was titrated rapidly with

0.1 N hydrogen bromide solution (prepared in acetic acid) to a bluish-green endpoint that stayed persisted for 30 s. The following equations [Equations (1)–(3)] were used to calculate the experimental oxirane oxygen content value (OOC_{exp}), theoretical OOC (OOC_{theo}), and relative percentage of conversion to oxirane (RCO), respectively.

$$OOC_{exp} = \frac{V \times N \times 1.60}{W_t} \quad (1)$$

Where:

V = Volume (mL) of the HBr titrant solution

N = Normality of the titrant.

W_t = Weight (g) of the sample.

1.6 = Atomic weight of oxygen divided by ten.

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

Where:

IV_o = Initial iodine value.

A_i = Atomic weight of iodine (gmol⁻¹)

A_o = Atomic weight of oxygen (gmol⁻¹)

$$RCO = \frac{OOC_{exp}}{OOC_{theo}} \times 100 \quad (3)$$

Where:

OOC_{exp} = Experimental OOC

OOC_{theo} = Theoretical OOC (max)

2.4 Determination of Iodine value (IV)

The iodine value (IV) of the sample was calculated according to the AOCS Official Method Cd 1–25 as explained by Yildiz *et al.* [41]. About 0.4 g sample was placed in a 500 mL flask. 15 mL carbon tetrachloride (CCl₄) was poured into the flask to dissolve the sample. 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% potassium iodide solution were added to the mixture. Titrant 0.1 N sodium thiosulphate solution was used to titrate the mixture until a yellow color titration indication was observed. Then, 1 ml 1% starch indicator solution was added. The titration was continued while the solution mixture was shaken vigorously until the blue color completely vanished at the titration endpoint. The

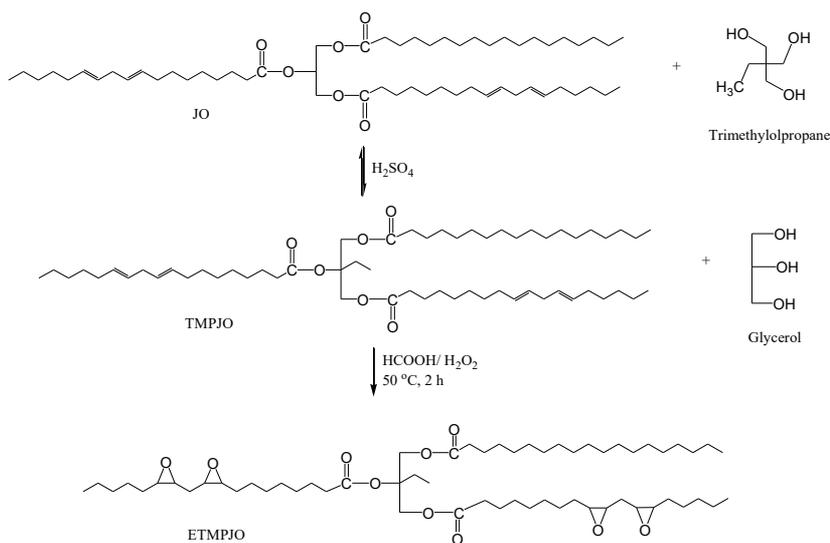


Figure 1: Preparation and epoxidation of TMPJO triester.

blank solution was treated under the same conditions. The IV was calculated by using Equation (4):

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

Where:

N = Exact normality of Na₂S₂O₃ solution (eq./L).

V_b = Volume (mL) of Na₂S₂O₃ solution used for blank titration.

V_s = Volume (mL) of Na₂S₂O₃ 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).

2.5 Structural characterization analysis

The molecular structure of *J. curcas* oil-based TMP triester (TMPJO) and its epoxide ETMPJO were analyzed using Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy, and the fatty acids and ester composition by gas chromatography. FTIR spectra were recorded on a Perkin Elmer Infrared Spectrophotometer in the range 400–4000 cm⁻¹. The ¹H and ¹³C NMR spectra were recorded on JEOL-ECP 400 spectrometer (400 MHz ¹H/100.61 MHz ¹³C) using CDCl₃ as a solvent.

3 Results and Discussion

3.1 Epoxidation reaction

The epoxidation process is aimed to improve the oxidative stability of TMPJO ester by removing the double bonds functionality. In this work, *J. curcas*-based TMP ester, TMPJO, was reacted with the epoxidation reagent of performic acid where in situ generated. The triacylglycerol (TAG) of *J. curcas* oil is best represented by the dominant TAG of palmitoyl-dilinoleoyl-glycerol, PLL, as JO composes 25.4% PLL. Figure 1 shows the transesterification of the represented TAG, PLL with TMP to produce TMPJO triester and followed by the epoxidation reaction of TMPJO to produce the epoxide TMPJO known as ETMPJO.

3.2 Optimization of the epoxidation reaction

J. curcas-based TMP triester (TMPJO) has the potential to be used for biodegradable biolubricants application [13], [14]. However, the TMPJO triester composes four double bonds that could reduce its specific lubrication properties of oxidation stability. Therefore, TMPJO was further modified by the epoxidation process to enhance its oxidative stability functionality. The epoxidation reaction involves the conversion of a double bond to epoxide or epoxy functionality. The

TMPJO triester initially shows an iodine value (IV) of 100 mg/g and the OOC_{theo} of 5.03%, respectively. After the epoxidation process, besides the high yield, the resultant ETMPJO should have no IV value, and its OOC should be as high as its OOC_{theo} value. Therefore, the important epoxidation parameters or reaction factors that affect the yield and the response parameters of IV and OOC should be optimized. The effects of parameters toward the epoxidation reaction were the molar ratio of double bond of TMPJO triester toward formic acid, and toward used hydrogen peroxide, the reaction temperature, and the reaction time. Response parameters of IV and OOC were used as benchmark for the efficiency of the epoxidation process of TMPJO. The optimization was carried out at the experiment condition at fixed reaction temperature and time of 50 °C for 2 h and varied the other parameters.

3.2.1 Effects of hydrogen peroxide molar ratio

The molar ratio of double bonds of TMPJO triester and formic acid was set 1: 1, and the molar ratio of hydrogen peroxide to the double bonds was varied at 1: 1, 1: 2, 1: 3, 1: 4, 1: 5, and 1: 6 to determine the effect of hydrogen peroxide to the double bonds. The response parameters of IV and OOC of the ETMPJO were monitored. The results are shown in Figure 2. The IV value of the ETMPJO triester was starting to reduce as the mole of hydrogen peroxide increased indicating that the epoxidation reaction was increasing. At the same time, the OOC_{exp} value start to increase as expected. The IV continued to reduce until it reached 15.8 mg/g at hydrogen peroxide mole of 2 and started to increase back as the hydrogen peroxide mole increased. The same trend for the OOC_{exp} value, increase to 3.53% at hydrogen peroxide mole of 2 and starts to decrease as hydrogen peroxide mole increase. Increasing the concentration of hydrogen peroxide created the condition where the performic acid catalyst was not generated further as the concentration of formic acid was limited. Furthermore, a strong oxidant, hydrogen peroxide, may oxidize the three-member oxirane ring or epoxy ring to be reopened back [2], [9]. As indicated earlier, the response parameters were optimum at hydrogen peroxide mole of 2 with lowest IV value and highest value of OOC_{exp} . At these points, nearly all double bonds were expected to be converted into the epoxy ring. Thus, it can be concluded that the

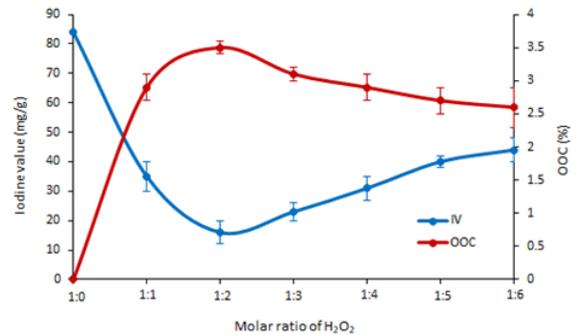


Figure 2: Effect of H₂O₂ molar ratio on OOC and IV values.

optimal molar ratio of H₂O₂ to the double bonds of TMPJO triester was at 2 mol with 81% of relative conversion oxirane, RCO efficiency.

3.2.2 Effects of formic acid molar ratio

The molar ratio of double bonds TMPJO triester to hydrogen peroxide (H₂O₂) was set at 1: 2, and molar ratio of formic acid to the double bonds of TMPJO triester was verified between 1: 0.5, 1: 1.0, 1: 1.5, 1: 2.0, 1: 2.5, and 1: 3.0. The same reaction response parameters of IV and OOC_{exp} were monitored. The results are shown in Figure 3. It can be observed that the higher the molar ratio of formic acid toward the double bonds of TMPJO triester, the lower the iodine value and the higher the OOC. When the molar ratio of formic acid increased to 2.0–3.0 mol, IV obtained was lower between 8.15–1.3 mg/g, and the OOC_{exp} was high between 4.0–4.38%. However, further increase in formic acid concentration will reduce the OOC_{exp} value. Increasing the concentration of hydrogen peroxide creating a more acidic medium at which a three-member oxirane ring an epoxy ring to be oxidized and reopened back [2], [9]. Once can conclude that at a molar ratio of formic acid of 2.5 mol, highest OOC_{exp} of 4.38%, and lowest IV value of 1.3 mg/g was the optimal condition with 81% RCO.

3.2.3 Effects of reaction temperature

The effect of epoxidation reaction temperature was studied at 30, 40, 50, 60, and 70 °C. The reaction conditions were set at a molar ratio of TMPJO triester double bonds: H₂O₂ was 1: 2, the molar ratio of double

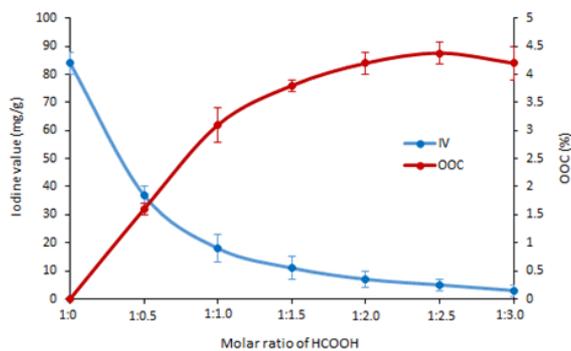


Figure 3: Effects of molar ratio of formic acid on OOC and IV values

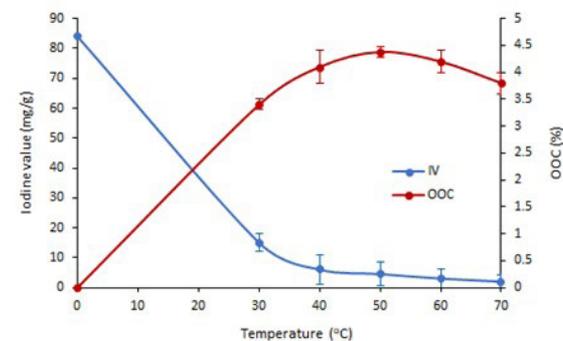


Figure 4: Effects of reaction temperature on OOC and IV values.

bonds of TMPJO triester: formic acid was 1: 2.5 2 h reaction time. The same reaction response parameters of IV and OOC_{exp} were monitored. The results are shown in Figure 4. It can be observed that the higher the reaction temperatures, the lower the IV and the higher the OOC values, respectively. Low IV and high OOC values when the reaction temperature was run at 30–50 °C and start to reduce as the temperature increases. This indicates that the epoxy ring was reopened or epoxide hydrolysis at a higher temperature. It can be concluded that at a reaction temperature of 50 °C, the highest OOC of 4.38% and lowest IV of 1.4 mg/g was the optimum reaction condition with 82% RCO.

3.2.4 Effects of reaction time

The reaction conditions were carried out at a molar ratio of double bonds of TMPJO triester to H_2O_2 of 1: 2, the molar ratio of double bonds of TMPJO triester to formic acid of 1: 2.5, and reaction temperature at

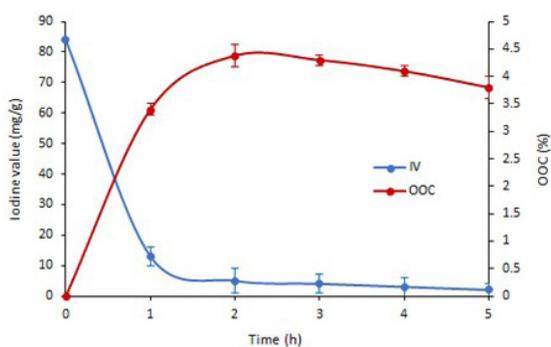


Figure 5: Effects of reaction time on OOC and IV values.

50 °C. The effect of the epoxidation reaction time was varied from 1, 2, 3, 4, and 5 h. The same reaction response parameters of IV and OOC_{exp} were monitored. The results are shown in Figure 5. Once can be observed that the IV and OOC_{exp} values dramatically reduced and increased at 1 h reaction time, respectively. As the reaction time further increased at 2 h, both reaction response parameters reached lower and higher values and remained slightly unchanged. The reaction time at 2 h showed the optimum value of IV at 1.4 mg/g and OOC at 4.38 with 87% RCO. It can be concluded that the optimal reaction conditions for the epoxidation reaction of TMPJO in this study were at molar ratio of double bond TMPJO: H_2O_2 of 1: 2, the molar ratio of double bond TMPJO: formic acid at 1: 2.5, reaction temperature and time at 50 °C and 2 hours, respectively. At this optimal condition, the resultant ETMPJO obtained was at 91% yield with a comparatively high relative conversion oxirane (RCO) of 87%. It contains a high OOC of 4.38% and a low IV of 1.4 mg/g.

3.3 Structural characterization analysis

3.3.1 Fourier transform infrared spectroscopy (FTIR)

The main functional groups present in the TMPJO triester and ETMPJO were the same ester moiety. The ester carbonyl $C=O$ was observed at 1741 cm^{-1} and ester $C-O$ (bending) at 1231 cm^{-1} , respectively. The important features in ETMPJO were the epoxy ring ($-\text{C}_2\text{C}_2-$) and the double bond of $-\text{C}=\text{CH}$ functional groups in TMPJO, respectively. The presence of two new peaks around 908 and 825 cm^{-1} , indicates an epoxy ring group ($-\text{C}_2\text{C}_2-$)

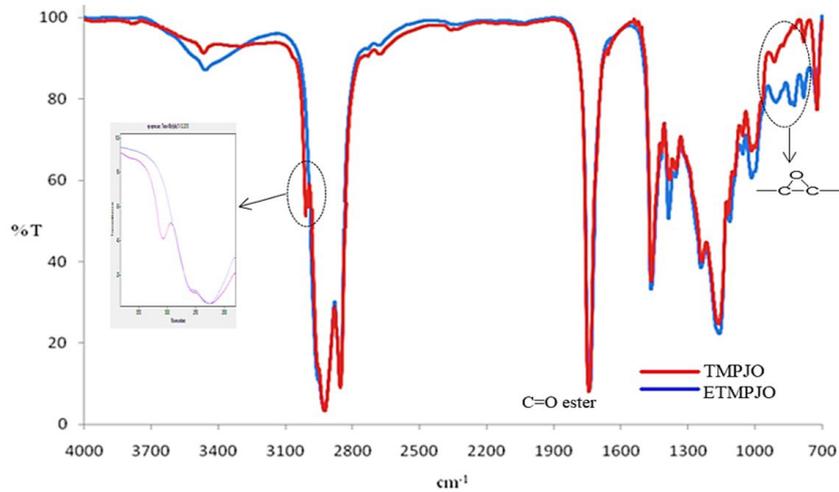


Figure 6: FTIR spectra of TMPJO and ETMPJO triester.

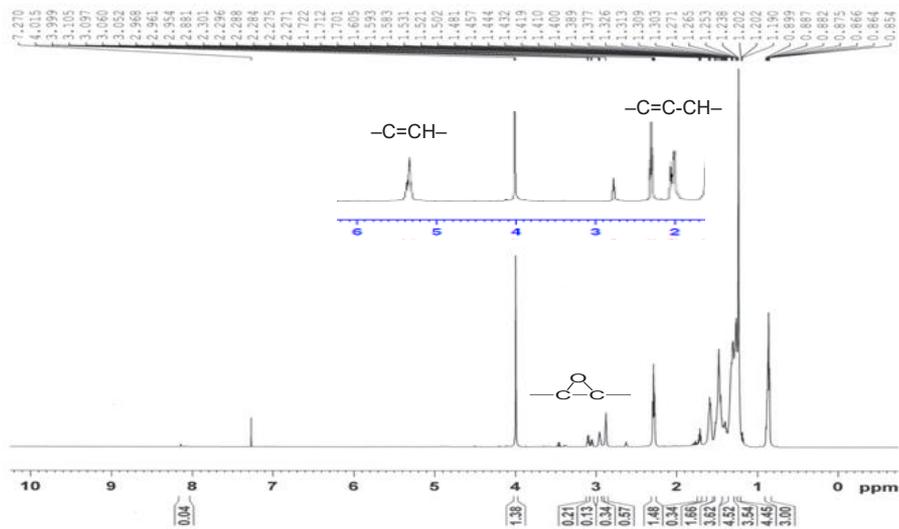


Figure 7: ¹H NMR spectra of TMPJO (inserted) and ETMPJO triester ester.

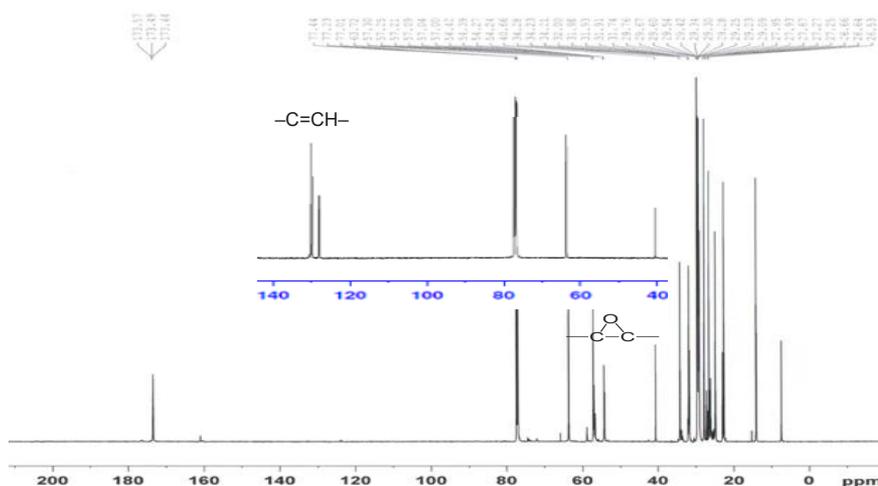
[42] in ETMPJO. At the same time, the disappearance of unsaturation double bond peak for TMPJO at 3004–3005 cm^{-1} as shown in Figure 6.

3.3.2 Nuclear magnetic resonance spectroscopy (NMR)

Once can be observed, the important NMR spectra feature changing for the conversion of TMPJO to ETMPJO. ¹H NMR spectra of TMPJO (small inserted) and ETMPJO triester are shown in Figure 7. The disappearance methylene proton signal (-CH=CH-)

of unsaturation functional group of TMPJO at 5.324–5.406 ppm, proton of -C=C-CH- at 1.97–2.09 ppm, and the appearance of proton signal at 2.881 ppm of an epoxide ring group (-C-C-) of ETMPJO have confirmed the epoxidation reaction successfully took place [40], [42].

Figure 8 shows the ¹³C NMR spectra of TMPJO (inserted) and ETMPJO triester. The presence of a signal at 54.24–57.30 ppm due to epoxide ring group (-C-C-) and the disappearance of the signal at 127.91–130.21 ppm belong to -C=C- of TMPJO ester have approved the ester formation [40] of ETMPJO.



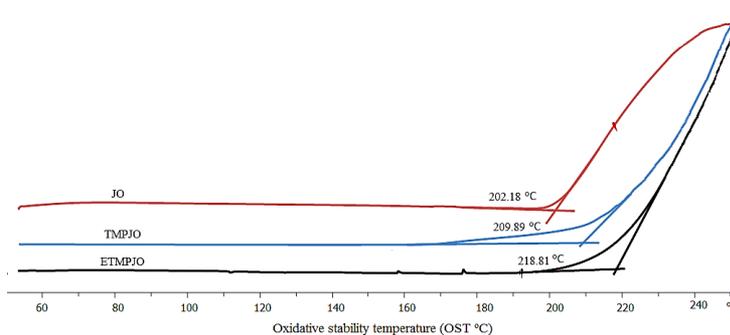


Figure 9: Oxidative stability temperature of *J. curcas* oil (JO), TMPJO, and ETMPJO triester.

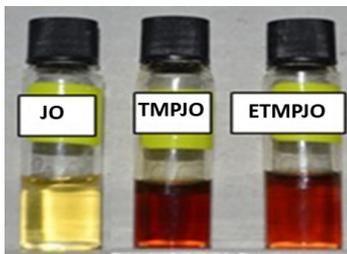


Figure 10: Photos of JO, TMPJO and ETMPJO triester.

4 Conclusions

The *in-situ* epoxidation of *J. curcas* oil-based trimethylolpropane ester (TMPJO) to produce epoxidized TMPJO (ETMPJO) was successfully carried out. Several reaction parameters such as the molar ratio of TMPJO towards hydrogen peroxide and formic acid, reaction temperature, and time were affected in the epoxidation process to produce ETMPJO with high yield, low IV, and high OOC_{exp} values. The spectroscopy studies (FTIR and NMR) have proved the conversion of TMPJO to ETMPJO with a good yield. ETMPJO yield obtained at the optimum conditions was 91% with relative conversion rate of (RCO) at 87%. ETMPJO has shown the chemical characteristic with low iodine value, and high oxirane oxygen content indicated that the epoxidation of TMPJO to produce ETMPJO was successfully converted with good yield. The ETMPJO has potential as commercial lubricant for the compressor oil industrial application. It is plausible that ETMPJO can be used as biolubricants or as an intermediate material to be further converted through ring-opening esterification with suitable branched alcohols or oleic acid to produce other high-end biolubricants for industrial application.

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