

EPOXIDATION OF JATROPHA METHYL ESTERS VIA ACIDIC ION EXCHANGE RESIN: OPTIMIZATION AND CHARACTERIZATION

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Abstract - Plant oils and their derivatives have been vigorously exploited as alternatives for synthesis of epoxides due to depletion of petroleum resources. In this study, crude jatropha oil (CJO) was subjected to a transesterification process to form jatropha methyl esters (JME) using peroxyacetic acid generated *in situ* from hydrogen peroxide and acetic acid via an acidic ion exchange resin (AIER). The effect of temperature, molar ratio of hydrogen peroxide to unsaturation, molar ratio of acetic acid to unsaturation, and catalyst loading were investigated. This study revealed that the maximum 89.9% relative conversion to oxirane rings was achieved after 6 h with the optimal reaction conditions of temperature at 70 °C, the molar ratio of hydrogen peroxide to unsaturation of 1.5 mol, the molar ratio of acetic acid to unsaturation of 0.5 mol, and catalyst loading of 16%. Fourier Transform Infrared (FTIR) spectra of the epoxidized jatropha methyl esters (EJME) showed oxirane peaks (doublet) at 825 and 843 cm⁻¹. ¹H NMR confirmed the diepoxide group at 2.85 ppm and 2.98 ppm, while the diepoxide signals of ¹³C NMR were present at 56.88-57.06 ppm. Production of bio-epoxides from Jatropha methyl esters hence looks promising with favorable physicochemical properties, availability, and versatility.

Keywords: Jatropha; Bio-epoxy resins; Epoxidation; FAME.

INTRODUCTION

Petroleum is the major source for production of polymers, plasticizers, lubricants, and others. The depletion of petroleum supply and the growing demand for new feedstock in many countries have encouraged researchers to find alternative resources. Plant oils and their derivatives have attracted the attention of researchers in various fields due to their availability, non-toxicity, and, most importantly, modifiability by chemical, physical, or enzymatic methods. Moreover, the usage of synthetic epoxy resin derived from petroleum raises many safety issues with regards

to health and environmental impacts. Bioresources derived from plant oil are an excellent substitute because they are available in abundance and green.

A plant oil derivative, Jatropha methyl esters (JME) have high iodine value which makes them suitable to be used as raw materials in the production of bio-epoxides. These epoxidized Jatropha methyl esters (EJME) with high oxirane value would be an excellent potential source for bio-epoxy resins.

Chemical modifications such as epoxidation are commonly used in synthesizing bio-epoxy resin or epoxide due to the ease of process handling at moderate conditions. It is described as the formation of an oxirane

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group by the reaction of peroxyacids and aromatic double bonds. Basically, this process is conducted with the presence of organic acid (formic or acetic acid), hydrogen peroxide, and catalysts (Campanella et al., 2008; Mushtaq et al., 2013; Latif et al., 2019). For instance, epoxidation by an environmental friendly AIER catalyst exhibits high selectivity and minimum side reactions.

The main content of a bio-epoxy resin is the oxirane ring, which is very reactive and enables epoxides to be used as biolubricants (Borugadda and Goud, 2015a), reactive diluents (Das and Karak, 2009), and stabilizers in PVC and plasticizers (Chua et al., 2012). Besides, they have also been used as intermediates in the production of polyols and polyurethanes (Chen et al., 2015). Production of bio-epoxy resins from plant oils has been reported previously from jatropha oil (Goud et al., 2010; Latif et al., 2019), rubber seed oil (Okieimen et al., 2005), cottonseed oil (Carbonell-Verdu et al., 2015), soybean oil (Cheng et al., 2015), sunflower oil (Benaniba et al., 2007), Karanja oil (Bajwa et al., 2016), and hemp oil (Cooney et al., 2011).

Not only plant oils have been used as raw material for the synthesis of biopolymers, their derivatives also have been gaining attention because of their excellent performances. A number of researchers have reported on epoxidation using derivatives of plant oils such as fatty acid methyl esters (Campanella et al., 2008), linoleic acid (Hong et al., 2015), and alkenes (Ghiron et al., 2005). FAME, otherwise is popularly known as biodiesel, currently has been used as an alternative for diesel fuel due to its special attributes, including that it is highly available, non-toxic and biodegradable (Satyanarayana and Muraleedharan, 2011; Kay and Yasir, 2012). It is produced from a transesterification process of triglyceride in crude plant oils with the assistance of alcohol and an acid or a base catalyst. Even though FAME has been used mainly in the automobile industry, the accessibility of its structure to undergo further chemical modifications such as the transformation of double bonds into oxirane ring units has opened a new dimension to oleochemical synthesis.

Many have reported on the production of bio-epoxides from crude jatropha oil (CJO) using epoxidation (Goud et al., 2010, 2007; Rios et al., 2011; Sammaiah et al., 2014; Latif et al., 2019). The factors affecting the process are reaction temperature, molar ratio hydrogen peroxide to unsaturation, molar ratio of organic acid to unsaturation, concentration of catalyst, and stirring speed. Instead of using CJO, this study focused on the use of jatropha methyl esters (JME) to produce bio-epoxy. Normally, epoxidized fatty acid derived from plant oils are found to have higher oxirane content, more reactivity, and lower viscosity compared to epoxidized crude oils (Wang and Schuman, 2012). This characteristic is very important in the production of epoxy. Table 1 shows a comparison of

Table 1. Comparison properties of CJO and JME.

Properties	CJO	JME
Density at 15 °C(kg/m ³)	918	880
Viscosity at 40 °C(mm ³ /s)	35.4	4.84
Acid value (mg KOH/g)	11.0	0.24
Iodine value	101	104
Saponification value	194	190

the properties of CJO and JME. JME possessed lower density and viscosity but higher reactivity than CJO (Bobade et al., 2013), and this makes it attractive for bio-epoxy production.

Up to date, no previous study has been reported on the epoxidation of JME resins. Therefore, the objective of this work was to investigate the reaction parameters affecting the epoxidation process of jatropha methyl esters. In addition, spectroscopic characterization such as FTIR and NMR were used to confirm the formation of epoxide groups in the epoxidized JME. Bio-epoxides produced through epoxidation of JME have potential as plasticizers and stabilizers in PVC, as bio-lubricants, and as a polymeric coating.

EXPERIMENTAL

Materials

Jatropha curcas seed oil used in this work was purchased from BATC Development Berhad (Bionas) and was used without further purification. Anhydrous methanol (CH₃OH), sulfuric acid (H₂SO₄), sodium methoxide (CH₃ONa), and anhydrous sodium sulfate (Na₂SO₄) were used during the transesterification process. These chemicals were purchased from R&M Chemicals Ltd. without further purifications. Hydrogen peroxide (50% H₂O₂) was purchased from Qrec Sdn Bhd, glacial acetic acid (CH₃COOH) from R&M, and Amberlite IR-120 from Sigma Aldrich.

Experimental setup and procedures

Production of jatropha methyl esters

Production of jatropha methyl esters was conducted using a transesterification method. Based on the preliminary tests, %FFA of crude jatropha oil was calculated to be 15.7% which was considered high. A high content of FFA creates a problem in the separation of the methyl ester layer from the glycerin fraction due to the formation of soap. Hence, a two-stage transesterification method was used (Deng et al., 2010; Jain and Sharma, 2010). The process was conducted in a 1000 mL three-necked flask completed with a mechanical stirrer, a reflux condenser, and a thermometer under atmospheric pressure. The experiment was performed at optimized conditions of methanol (CH₃OH), sulfuric acid (H₂SO₄), and sodium methoxide (CH₃ONa) adapted from Rashid et al. (2012). The molar ratio of methanol to oil was reported to be optimum at 6:1 and percentage weight

of catalyst is 1% (w:w) of oil. Other than the optimal values, the reaction is incomplete and leads to soap formation (Rashid and Anwar, 2008)

Percentage weight of obtained methyl esters was calculated using the equation below:

$$\text{Biodiesel yield (wt\%)} = \frac{\text{gram of methyl esters produced}}{\text{gram of jatropa oil used in production}} \times 100 \quad (1)$$

The obtained methyl esters were subjected to physicochemical tests as well as FTIR and NMR analysis to confirm the formation of methyl esters and removal of glycerol. Methyl esters were stored for further used in the epoxidation process.

Epoxidation of jatropa methyl esters

Epoxidation reaction was carried out in a three-necked round-bottom flask (1000 mL), equipped with a mechanical stirrer, and placed in a water bath which could be controlled to within + 1 °C of the desired temperatures. A separatory funnel was inserted in the left neck to add dropwise the hydrogen peroxide. After the addition of the hydrogen peroxide completed, it was replaced with a thermometer to record the temperature of the epoxidation process. Another neck was sealed and opened intermittently for sample withdrawal.

The epoxidation method of Goud et al. (2006) was adopted for all of the experiments. An appropriate mass of JME (239.23 g) was added in the flask with the necessary amount of acetic acid (0.5 mol) and Amberlite (16%) catalyst based on the percentage weight of organic phase (oil and acetic acid) (Borugadda and Goud, 2015a). The mixture was subjected to continuous stirring for 30 min, followed by addition of 30% of hydrogen peroxide (1.5 mol). Hydrogen peroxide was added to the flask drop-wise within half an hour. After the addition of hydrogen peroxide was completed, the reaction was continued for 10 h. The rapid stirring was maintained throughout the experiments so that a fine dispersion of oils was achieved. At 1-h intervals, 50 mL of mixture was drawn off using a 50 mL glass pipette. When the addition of hydrogen peroxide was completed, time was set to zero.

The collected samples were placed in a 50 mL separatory funnel and the bottom layer which consisted of acetic acid, hydrogen peroxide, and Amberlite, was drawn off. The purification process of the upper layer (bio-epoxy resins) was conducted using 5% diethyl ether together with warm and cold water. First, the resin was washed with successive portion of diethyl ether, followed by cold water and finally, hot water with the purpose to remove residual fatty acid or unreacted chemicals. The solution was dried over anhydrous sodium sulfate (1.5% w:w) overnight in an oven at 70 °C to remove any traces of water. All

samples were collected in 5 mL glass vials and sent for oxirane content analysis.

Analytical methods

Oxirane Oxygen Content

The determination of relative conversion to oxirane was necessary to determine the quality of oxirane as well as the efficiency of the epoxidation process. The oxirane content of each sample was determined using the direct method with hydrobromic acid solution presented by Paquot (1979). From the oxirane content, the percentage relative conversion to oxirane was determined using the following formula:

$$\text{Relative conversion to oxirane (\%)} = \frac{O_{\text{exp}}}{O_{\text{theo}}} \times 100 \quad (2)$$

where O_{exp} and O_{theo} are the experimental and theoretical oxirane oxygen values (%) respectively. O_{theo} is determined using the following equation:

$$O_{\text{theo}} = \left[\frac{\left(\frac{IV_0}{2A_i} \right)}{100 + \left(\frac{IV_0}{2A_i} \right) (A_0)} \right] \times A_0 \times 100 \quad (3)$$

where A_i (126.9) and A_0 (16.0) are the atomic weights of iodine and oxygen, respectively, and IV_0 is the initial iodine value of the oil sample.

FTIR Spectroscopy Analysis

The Fourier Transform Infrared (FTIR) analysis was carried out to determine the functional group in the CJO, JME, and EJME. The spectra were recorded on an FTIR Perkin-Elmer spectrophotometer model Spectrum-1000 (Perkin-Elmer, Norwalk, CT, USA). A potassium bromide (KBr) pallet was used to determine the background signal. The spectra were obtained over the frequency range 4000-650 cm^{-1} at the resolution of 4 cm^{-1} and the final output was in % transmittance.

NMR Spectral analysis

The NMR samples were prepared by dilution with deuterated chloroform at a ratio 1:1 by volume and analyzed in 5 mm NMR tubes. NMR spectra were recorded on a JEOL-ECP 500 NMR spectrophotometer operating at 400.13 MHz. The results were analyzed using Delta 5.0.4 software.

RESULTS AND DISCUSSION

Physicochemical tests were conducted and the results for all three samples of CJO, JME, and EJME are shown in Table 2. The iodine value of JME was

Table 2. Physicochemical characteristic of CJO, JME and EJME.

Properties	CJO	JME	EJME
Iodine value (g I ₂ /100 g)	103.1±0.6	107.7±1.4	9.9±0.9
Acid value (Mg KOH/g)	15.7±0.7	0.84±0.1	-
Free fatty acid (%)	7.89±0.7	0.42±0.1	-
Saponification value (Mg KOH/g)	185.6±2.2	175.31±3.2	-
Density at 30 °C (kg/m ³)	893±1.8	868±0.9	920±1.5
Dynamic viscosity at 30 °C (cP)	46.8±0.7	5.7±0.5	11.55±0.6
Kinematic viscosity at 30 °C (mm ² /s)	52.41±0.8	6.56±0.6	12.55±0.7
Specific gravity	0.89±1.8	0.87±0.9	0.92±1.5

within the same range as CJO because there was no reduction or addition of double bonds during transesterification, only glycerol was removed from the triglycerides. The viscosity of JME and EJME were very low compared to CJO, which was due to the formation of monoglycerides in JME and oxirane rings in EJME. The acid value and FFA for JME reduced to 0.84±0.1% and 0.42±0.1%, respectively, because of the pretreatment steps. This reduced the JME saponification value to 175.31±3.2 mg KOH/g. Similar results have been reported by previous works (Lu et al., 2009). Highest percentage yield of JME obtained was 90.6±1% with a total reaction time of 4 h. JME had lower density and viscosity compared CJO due to the removal of glycerol. However, the density of EJME was higher than CJO and JME due to the formation of oxirane rings. The viscosity of EJME was also slightly higher than JME but was still lower than CJO. Fatty acid composition of methyl esters was as follows: C16:0 = 15.1%, C18:0 = 9.9%, C18:1 = 41.7%, C18:2 = 31.0%.

Epoxidation reactions catalyzed by AEIR using peroxyacetic acid generated *in situ* were conducted to investigate the effect of four main reaction variables on the epoxidation process. The studied variables were reaction temperature and time, molar ratio of hydrogen peroxide to unsaturation, molar ratio of acetic acid to unsaturation, and catalyst loading. Graphs of relative conversion to oxirane (RCO) with respect to reaction time were plotted for each variable.

Effect of reaction temperature

Temperature plays the most important role in the epoxidation reaction (Campanella et al., 2008) and the effect of temperature on the epoxidation process was investigated at 30, 50, 70, and 85 °C. The results of relative percentage conversion to oxirane were demonstrated in Fig. 1. RCO increased linearly with time before it gradually decreased. As shown, the rate of epoxidation increased when the temperature increased from 30 °C to 85 °C. At a reaction temperature of 30 °C, the highest RCO of 54.8% was obtained when the experiment was conducted for 8 h. As the reaction temperature was increased to 50 °C, RCO increased to 68.3% and the reaction time was reduced to 7 h. A reaction temperature of 70 °C was concluded to be

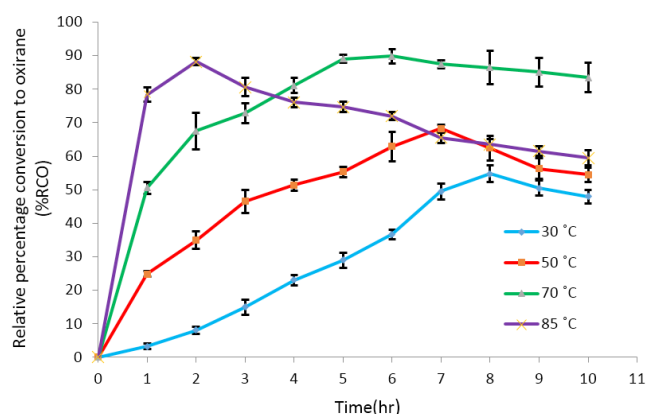


Figure 1. Effect of reaction temperature on relative percentage conversion to oxirane. Reaction conditions: JME, 1 mol; HP to unsaturation molar, 1.5:1; AA to unsaturation molar ratio, 0.5:1; catalyst loading, 16%; stirring speed, 1500 rpm.

the optimal condition because it provided the highest RCO (89.8 %) in the shortest time, which was 6 h.

A similar optimum reaction temperature was reported by Goud et al. (2007) with 88% of RCO. As shown, the RCO for reaction condition at 85 °C decreased rapidly after it reached a maximum point of 88.2% after 2 h. A higher reaction temperature promotes more oxirane cleavages to occur, which then leads to the formation of glycol in the final product (Dinda et al., 2008; Mungroo et al., 2008). At a high reaction temperature, water which was the product of the reaction between hydrogen peroxide and acetic acid can initiate oxirane ring cleavage with acetic acid and later form hydroxyl groups on the fatty ester backbone (Saithai et al., 2013). High temperature promotes hydrolysis (oxirane cleavage), which was indicated by the formation of glycol (Goud et al., 2007; Goud et al., 2006; Mungroo et al., 2008). Percentage of conversion to glycol in the final product can be calculated using the method by May (1973). Moreover, the formation of glycol can be verified using FTIR and NMR analysis. From Fig. 1, it can be concluded that the time required to attain the maximum RCO was different for each reaction temperature. It was agreed that moderate reaction conditions were more favorable to attain the maximum yield with minimum impurities (Goud et al., 2006).

Effect of molar ratio of hydrogen peroxide to unsaturation

The role of hydrogen peroxide is directly associated with acetic acid in the formation of peroxyacetic acid. However, its role is more significant because it is consumed during the reaction, but acetic acid is regenerated after their oxygen atom is utilized (Goud et al., 2010; Mushtaq et al., 2013).

The effect of hydrogen peroxide to ethylenic unsaturation molar ratio on the epoxidation process was studied at 0.8, 1.1, 1.5, and 2.0 mol of hydrogen peroxide for 1 mol of JME. As shown in Fig. 2, RCO initially increased with the increasing molar ratio. When the molar ratio was increased from 0.8 to 1.1, the rate of epoxidation increased progressively, indicated by the RCO increase from 75.9% to 88.95%. Further increment of the molar ratio to 1.5 mol gave the highest RCO of 89.6% at 6 h. When the experiment was conducted at a higher molar ratio, the rate of epoxidation increased higher than that of 1.5 mol reaction from 0 to 2 h but only achieved the highest RCO of 88.5% at 5 h, which is less than the 1.5 mol reaction.

After the reaction was extended further, RCO was observed to decrease due to oxirane cleavage. Hence, the optimal condition for molar ratio of hydrogen peroxide to ethylenic unsaturation was concluded to be 1.5 mol. Sinadinović-Fišer et al. (2012) had reported similar molar ratio of hydrogen peroxide as the optimal value, with lower RCO, 78.3%, at a longer reaction time of 8 h. This may be due to the feedstock used, which was crude Jatropha oil, while in this reaction, Jatropha methyl esters were used instead. The RCO value decreased to 88.5% after the molar ratio was increased to 2 mol. This was because a higher hydrogen peroxide concentration promoted the acceleration of oxirane ring opening, which led to the poor stability of the final product (Goud et al., 2006).

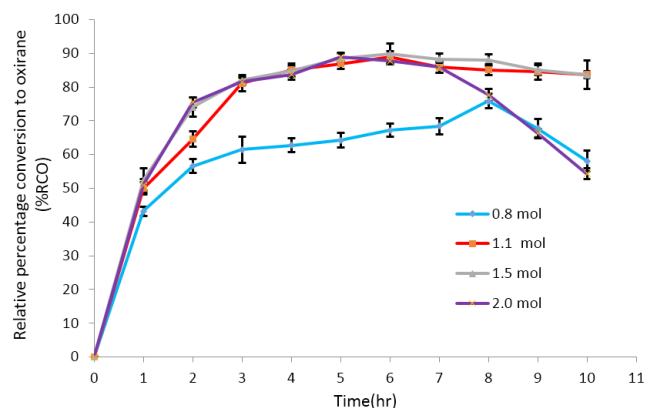


Figure 2. Effect of hydrogen peroxide per mole of ethylenic unsaturation on relative percentage conversion to oxirane. Reaction conditions: JME, 1 mol; AA to unsaturation molar ratio 0.5:1; catalyst loading 16% of oil; temperature 70 °C; stirring speed 1500 rpm.

Effect of molar ratio of acetic acid to unsaturation

Acetic acid is a better oxygen carrier compared to formic acid (Dinda et al., 2008; Goud et al., 2007; Mungroo et al., 2008); hence, acetic acid was chosen as the oxygen carrier in this reaction. The effect of acetic acid to ethylenic unsaturation molar ratio on the epoxidation process was studied at 0.3, 0.5, 0.65, and 1.0 mol. As shown in Fig. 3, the rate of epoxidation increased significantly when the molar ratio was increased from 0.3 to 0.5 mol. Highest RCO was obtained at 0.5 mol with the value of 89.9% at 6 h. After the molar ratio was increased to 0.65 and 1 mol, the rate of epoxidation increased and highest RCO was achieved faster than that at 0.5 mol reaction. However, as depicted in Fig. 3, RCO was reduced to 88.5%. As a conclusion, the rate of the epoxidation reaction increased with increasing acid concentrations, resulting in a higher conversion of double bonds to oxirane ring. At the same time, the increased acid concentration can also lead to the destruction of oxirane rings, thereby reducing epoxidation yield. The optimal molar ratio of acetic acid was identified to be 0.5 mol to ethylenic unsaturation, which was similar with previous reports (Goud et al., 2010; Sinadinović-Fišer et al., 2012).

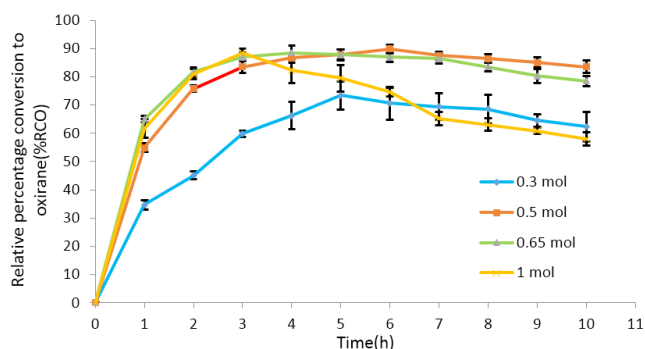


Figure 3. Effect of acetic acid per mole of ethylenic unsaturation on relative percentage conversion to oxirane. Reaction conditions: JME 1 mol; HP to unsaturation molar ratio 1.5:1; catalyst loading 16%; temperature 70 °C; stirring speed 1500 rpm.

Effect of catalyst loading

Amberlite IR-120 is among the best heterogeneous catalyst with high selectivity to the formation of epoxides and high oxirane conversion (Borugadda and Goud, 2014). The effect of catalyst loading on the epoxidation process was studied at 5%, 10%, 15%, and 20%. Fig. 4 shows the results obtained for the variations of catalyst loading. An increase in catalyst loading leads to an increase in both total active volume and total surface area of the catalyst. Hence, it increased the rate of in situ peroxyacetic acid formation.

It was observed that an increase in catalyst loading resulted in an increase in the initial rate of epoxidation as well as an increase in RCO. As shown in Fig. 4, the rate of epoxidation reaction increased when the

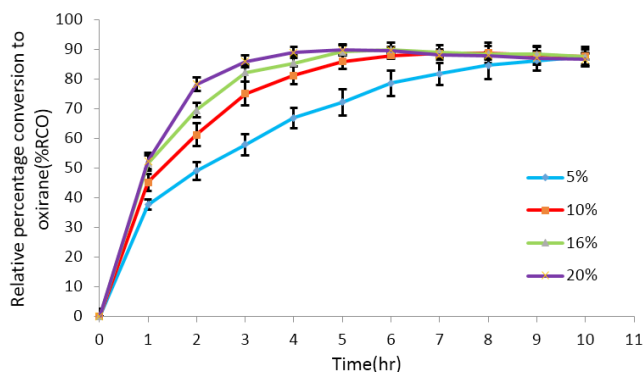


Figure 4. Effect of catalyst loading on relative percentage conversion to oxirane. Reaction conditions: JME, 1 mol; HP to unsaturation molar ratio, 1.5:1; AA to unsaturation molar ratio, 0.5:1; temperature, 70 °C; stirring speed, 1500 rpm.

percentage of catalyst was increased from 5% to 20%. The lowest rate was achieved at 5% with the maximum RCO of 87.5% was obtained at 10 h as indicated in the graph. Further increase of the catalyst concentration to 10% increased the RCO to 88.7% at 8 h. Maximum RCO was achieved at 16% catalyst loading. At similar reaction conditions, Goud et al. (2007) reported that 16% of catalyst loading attained 88% yield. Hence, it was concluded that 16% was the optimal condition for catalyst loading.

Since the AIER has been reported to affect the selectivity, it is desirable to study the epoxidation of JME in bulk with an objective of obtaining higher oxirane selectivity compared to homogenous catalyst (Goud et al., 2007). High catalyst loading does not affect the production cost because the catalyst can be recovered from the final product and recycled. A

report by Mungroo et al. (2008) stated that, at the end of the reaction, the catalyst was removed by filtration and washed with water and diethyl ether. The washed catalyst was air-dried and reused. This clearly indicates that the heterogeneous catalyst, AIER, can be recycled with little loss of activity. In this study, the recovery method of the catalyst is very simple using filter paper. The low viscosity of EJME accelerates the recovery process to less than 1 h.

FTIR analysis

The spectroscopic properties of CJO, JME, and EJME were studied by FTIR spectroscopy. FTIR is a sensitive technique appropriate to monitor the formation of FAME and oxirane ring in transesterification and epoxidation processes, respectively. FTIR spectra demonstrated the presence of peaks in the range of 3002-3008 cm^{-1} associated with the stretching of C-H attached to double bonds. As can be seen from Fig. 5, the presence of unsaturation in both CJO and JME was confirmed by the presence of a peak at 3009 cm^{-1} .

The formation of oxirane ring after the epoxidation process was also demonstrated in Fig. 5. It can be observed by the disappearance of the peak at 3009 cm^{-1} in JME and the appearance of oxirane peaks (doublet) at 825 and 843 cm^{-1} . This was in accordance with the reports of previous works, that oxirane ring exists in the range of 820 to 843 cm^{-1} (Petrovic et al., 2002; Saremi et al., 2012; Borugadda and Goud, 2014). Moreover, FTIR was not only used to monitor the formation of oxirane ring, but also to monitor the formation of any side reactions such as oxirane ring opening (Borugadda and Goud, 2015b).

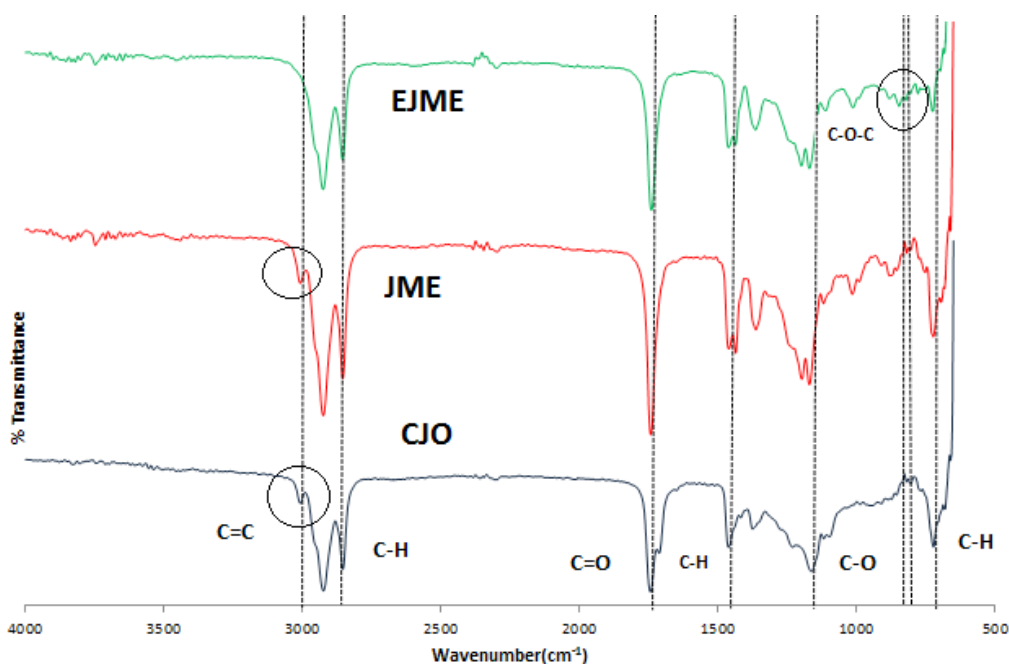


Figure 5. FTIR spectra of CJO, JME and JME epoxide.

The absence of hydroxyl peaks in the range of 3000-3500 cm^{-1} (O-H range) proved that minimum oxirane cleavage had occurred in the epoxidation process at optimum conditions. This result agreed with an investigation conducted by Hong et al. (2015) which mentioned that to optimize epoxidation yield, hydroxyl and unsaturation peak must not appear in the FTIR spectrum.

NMR spectral analysis

^1H NMR

Nuclear magnetic resonance spectroscopy technique is a technique used to determine a compound's unique structures by identifying a carbon-hydrogen framework of an organic compound. ^1H NMR spectroscopy of crude oil indicated the appearance of glycerol and unsaturation in certain peaks. Glycerol is removed during the transesterification process producing methyl esters.

The spectrum of CJO, which consists mainly of triglycerides, was generated as a baseline prior to reaction. The spectrum associated with a typical glyceride profile was compared with previous works (Kouame et al., 2012; Mushtaq et al., 2013). The spectrum of CJO showed the existence of unsaturation in the range of 5.27-5.32 ppm and 2.00 ppm and glycerol in the range of 4.0-4.27 ppm. Analysis of methyl esters shows the existence of ester peak and unsaturation, but not a glycerol peak. Formation of methyl esters was confirmed by the removal of glycerol, indicated by

the disappearance of glycerol peaks at 4.07-4.28 ppm and the presence of ester peak at 3.61 ppm. After the synthesis of epoxides, the formation of products was confirmed by the disappearance of unsaturation peaks and the appearance of epoxy peaks (Fig. 6).

The ^1H NMR analysis confirmed the presence of di-oxirane rings at 2.85 ppm and 2.98 ppm. Moreover, unsaturation peaks were also observed to be absent in the EPJME spectrum, at 2.003 ppm and 5.27-5.32 ppm. Similar result was reported by Borugadda and Goud (2014) during their study on the epoxidation of castor oil FAME.

^{13}C NMR

In ^{13}C NMR analysis, unsaturation peaks existed in the range of 127.95-130.17 ppm in both CJO and JME. The characteristic peaks of ester carbonyl (-COO-) and C-O at 174.23 ppm and 51.36 ppm, respectively, were observed in the spectrum of the JME. The peaks in the range of 29.20-34.09 ppm are from the methylene carbons of the long carbon chain in FAME. A study on transesterification of jatropa oil by Ahmed et al. (2015) presented identical results and concluded that jatropa biodiesel is formed. As shown, unsaturation peaks were observed to be absent in the EPJME spectrum and new peaks present around 56.88-57.06 ppm were identified as the oxirane rings (Fig. 7). However, traces of unsaturation were still present with a peak at 123.96 ppm, in accordance with the percentage conversion which was around 90.8%.

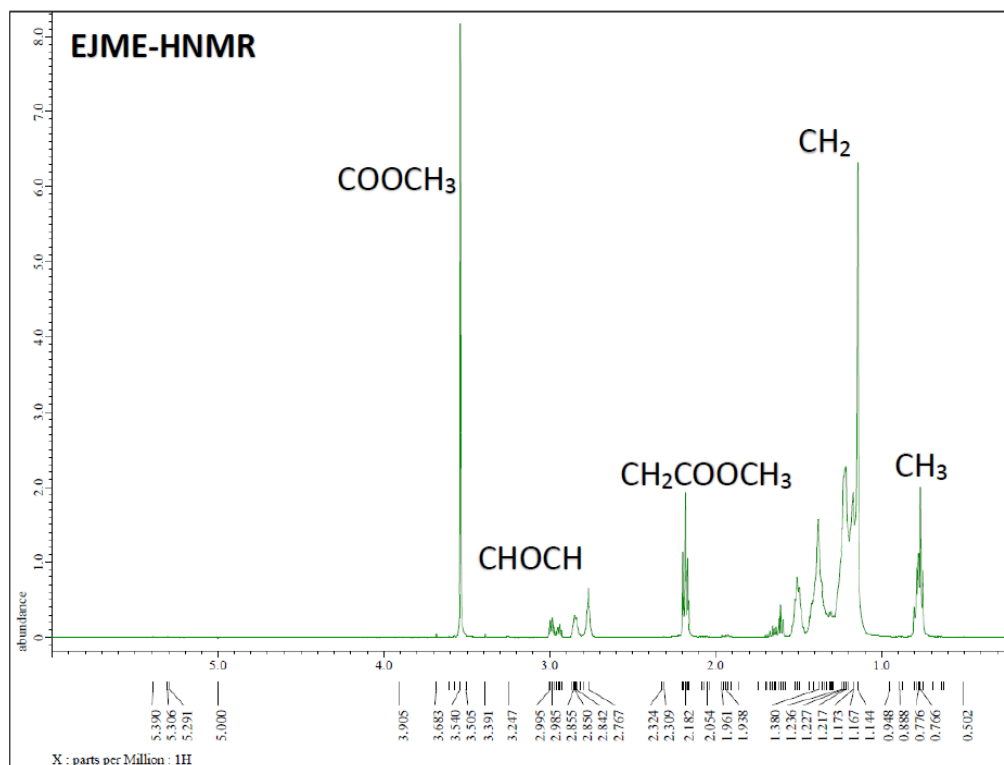


Figure 6. ^1H NMR spectra of EJME.

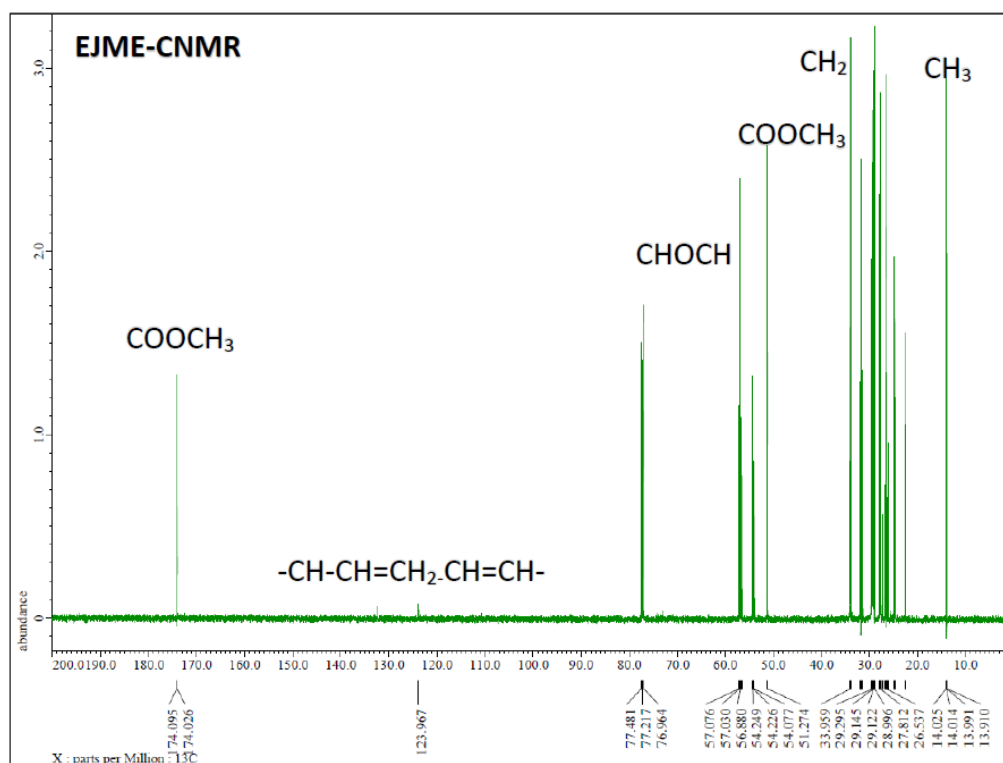


Figure 7. ^{13}C NMR spectra of EJME.

CONCLUSIONS

The epoxidation of jatropha methyl esters was carried out successfully using peroxyacetic acid generated *in situ* catalyzed by acidic ion exchange resin. Jatropha methyl esters are a promising alternative in the production bio-epoxides because of their physicochemical properties, availability, and versatility. It was found that the epoxidation reaction occurred optimally at a reaction temperature of $70\text{ }^{\circ}\text{C}$ for 6 h with an acetic acid to unsaturation ratio of 0.5:1, a hydrogen peroxide to unsaturation ratio of 1.5:1, and a catalyst loading of 16% from the total organic phase. Under these optimum conditions, 89.9% conversion of unsaturation to oxirane was achieved. Not only did AIER provide a greener alternative for the epoxidation process, but it was also easily separated from the final product. The formation of epoxide was confirmed by FTIR and NMR spectral analysis. Based on the relative conversion to oxirane, it can be concluded that new value-added products such as bio-epoxy resins can be produced from jatropha methyl esters.

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ABBREVIATIONS

AIER	Acidic Ion Exchange Resin
CJO	Crude jatropha oil
^{13}C NMR	Carbon Nuclear Magnetic Resonance
EJME	Epoxidized jatropha methyl esters
FTIR	Fourier Transform Infrared Spectroscopy
^1H NMR	Proton Nuclear Magnetic Resonance
JME	Jatropha methyl esters
RCO	Relative conversion to oxirane

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