Epoxidation of castor oil fatty acid methyl esters (COFAME) as a lubricant base stock using heterogeneous ion-exchange resin (IR-120) as a catalyst

Venu Babu Borugadda, Vaibhav V Goud*

*Department of Chemical Engineering, Indian Institute of Technology, Guwahati, Guwahati -781039, Assam, India

Abstract

Castor oil fatty acid methyl esters (COFAME) epoxide was derived by In-situ epoxidation reaction from COFAME to be used as a bio-lubricant base stock. During the reaction acetic acid was acted as an active oxygen carrier and hydrogen peroxide (H₂O₂) was an oxygen donor in the presence of strongly acidic cation ion-exchange resin (Amberlite IR 120) as a heterogeneous catalyst. In-situ epoxidation reaction was carried out at H₂O₂, acetic acid to ethylenic unsaturation molar ratio of 1.5 and 0.5 respectively; catalyst loading 15 wt%, reaction temperature 60 °C and reaction time 10 h. The objective of the study was to improve the thermo-oxidative stability of epoxidised COFAME. The resulting products were confirmed by ¹H NMR, FTIR spectroscopy and also analysed for oxirane oxygen content (OOC). Required physico-chemical properties were estimated for unmodified COFAME and epoxidised COFAME. Thermo-oxidative stability of epoxide was determined by thermo gravimetric analysis (TGA) technique in an inert and oxygen atmosphere. Thermo-oxidative stability of COFAME and its epoxide was compared with conventional servo hydraulic lubricant base stock oil. The present work has clearly illustrated significant improvement in the thermo-oxidative stability of COFAME epoxide i.e. after the structural modification.

Keywords: Castor oil fatty acid methyl esters (COFAME); epoxidation; oxirane oxygen content (OOC); TGA; ion-exchange resin.

© 2014 Vaibhav V. Goud. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Selection and peer-review under responsibility of Organizing Committee of ICAER 2013

* Corresponding author. Tel: (0361) 2582272, Fax: (0361) 2582291.
E-mail address: vvgoud@iitg.ernet.in
1. Introduction

Since the ancient days lubricants are serving great applications in automobiles industries, transmission and aviation machinery. Lubricants are playing critical functions such as reducing friction by improving the smoothness between two moving surfaces, minimising the generation of heat due to friction, increasing the efficiency and minimising energy losses. Currently, the most common types of lubricant base oils available in the market are automotive transmission fluids, metal working fluids, hydraulic fluids, cold rolling oils, fire resistant hydraulic fluids, industrial gear oils and neat cutting oils [1-3]. These fluids are originated from mineral oils, synthetic oils and re-refined oils. Among the available lubricant base oils mineral oils are the most commonly used and conventional ones; they consist predominantly of hydrocarbons but also contain some sulphur and nitrogen compounds with traces of a number of metals.

It has been figured out that, around 5-10 million tons of fossil originated products are entering into the environment every year via volatility, accidental spillage, total loss applications, non-recoverable usage, industrial and municipal wastes, urban runoff and refinery process; said paths are a root cause to pollute the environment [4]. It was reported that conventional lubricant base stocks are highly toxic to the eco-system and exhibits poor biodegradability [5]. In addition to that, since the last decade gradual dwelling of world fossil reserves, insufficient supply, high demand for the consumption and sudden hike in the prices of fossil fuels made the consumers and researchers to think about the alternative feed stocks which are cost effective. Due to the aforesaid negative impacts of mineral oils on ecosystem lubricant industry has been trying to formulate renewable, biodegradable lubricants with similar or even better technical characteristics than those originated from mineral oils. When the researchers were looking forward for the renewable resources, vegetable oils drew much attention as a replacement to fossil fuels because they are renewable and biodegradable [6, 7].

Vegetable oils also show most of the specific properties required for lubricant applications such as high viscosity index, high lubricity, higher flash point, very low volatility due to high molecular weight of the triacylglycerols. On the contrary, they posses low thermal, oxidative stabilities and poor low-temperature characteristics, which are mainly due to the presence of unsaturation in their fatty acid composition. Transformation of unsaturated double bonds (C=C) in to oxirane ring via epoxidation received special attention to synthesize bio-lubricant base stock, because it opened up a wide range of feasible reactions that can be carried out under moderate reaction conditions due to high reactivity of oxirane ring [8, 9]. Reported literature on synthesis of bio-lubricant revealed that, in most of the studies edible oils are used for biolubricant synthesis and very scanty information is available on the use of non edible oil. In this regard, the main objective of this study was to develop new environmental friendly biolubricant base stock with improved thermo-oxidative stability by epoxidising the castor oil fatty acid methyl esters (COFAME) using acidic ion-exchange resin as a heterogeneous catalyst. This study was also intended to determine and investigate the physico-chemical properties of epoxidised COFAME (structurally modified) and COFAME. Finally, the obtained results were compared with the conventional hydraulic grade lubricant from servo.

2. Materials and methods

Mechanically extracted castor oil was collected from Cherukupalli (Guntur Dist), Andhra Pradesh, India. Hydrogen peroxide (purity = 50% v/v) was purchased from RANKEM, ion exchange resin (Amberlite IR 120, strong acid), methanol, potassium hydroxide pellets and glacial acetic acid (purity = 99-100%) was supplied by Merck India Ltd. All the other reagents used for analysis were analytical grade and were used without any further purification.

The physico-chemical properties of COFAME and its epoxide were determined according to ASTM and AOCS official methods, details about the standards are reported in results and discussions. Theoretical oxirane oxygen (OOh) and relative percentage conversion to oxirane was calculated from the following expressions
\[ OO_{the} = \left[ \frac{IV_0 / 2A_i}{100 + (IV_0 / 2A_i)A_0} \right] A_0 \times 100 \]  

(1)

Where \( A_i \) (126.9) and \( A_0 \) (16) are the atomic weights of iodine and oxygen respectively, and \( IV_0 \) is the initial iodine value of the COFAME.

Relative percentage conversion to oxirane = \[ \frac{OO_{exp}}{OO_{the}} \times 100 \]  

(2)

Where \( OO_{exp} \) is the experimentally determined content of oxirane oxygen and \( OO_{the} \) is the theoretically maximum oxirane oxygen in 100g of COFAME epoxide.

2.1. \(^1\)H-NMR spectroscopy

\(^1\)H NMR spectrum of COFAME and its epoxide was recorded using 500 MHz NMR spectrometer (Oxford, AS400, China) using a 5 mm broad band inverse probe head equipped with shielded z-gradient accessories. Samples were dissolved in 400 \( \mu \)l deuterated chloroform (CDCl\(_3\)) and transferred to 5-mm NMR tube. The deuterated chloroform chemical shift peak at 7.26 ppm was considered as internal reference. Typical parameters used were: spectral width: 4800 Hz; time domain data points: 32 K; flip angle: 90°; relaxation delay: 5s; spectrum size: 32 K points; and line broadening for exponential window function; 0.3 Hz.

2.2. Fourier transformed infrared spectroscopy (FTIR)

FTIR spectra of the initial raw material and final product were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (IR Affinity 1, Shimadzu, Japan) in the range of 400 – 4000 cm\(^{-1}\). Very thin film of KBr pellet was prepared to introduce the sample for spectral analysis. The spectra were recorded in transmittance mode.

2.3. Thermo gravimetric analysis (TGA)

Thermo gravimetric technique evaluates the variation in weight loss as a function of temperature. In the present study, thermo-oxidative stability of COFAME and its epoxide was studied by varying the temperature from ambient to 700°C. The non-isothermal thermo gravimetric analysis was performed in TG/SDTA851e model (METTLER TOLEDO). To obtain the thermal stability, samples were heated in nitrogen (40 ml/min) atmosphere from ambient to 700 °C at constant heating rate of 10°C/min, similarly to determine the oxidative stability oxygen (100 ml/min) atmosphere was used as a reactive gas along with the nitrogen as purging gas. Different amount of samples were used during the analysis, but all the samples were measured in mg in an open silica crucible (less than 10mg), TG curves as well as its derivative curves were used to analyze the onset temperature of the ester and its epoxide.

3. Synthesis methyl esters and epoxides

3.1. Alkali-catalyzed transesterification of castor oil (CO)

Since the FFA value of CO was less than unity, single step base catalysed transesterification reaction was carried out. The detailed experimental procedure, purification of the product and its fatty acid composition was clearly reported in our earlier communication [10]. The end product was used as a raw material to synthesise the castor oil fatty acid methyl esters epoxide.

3.2. Epoxidation of COFAME

COFAME epoxidation reaction was carried out in an isothermal, mechanically stirred (five bladed turbine type), cylindrical flat bottom three necked glass reactor (250 ml) The entire setup was immersed in heating water bath.
During the experiment COFAME, hydrogen peroxide and acetic acid quantities were used in molar ratio (1:4:0.5); ion-exchange resin (IR-120) was consumed in terms of weight percentage (15%). Initially 50 g of COFAME (0.29 mol) was heated to reaction temperature (60 °C), glacial acetic acid 8.96 g (0.5 mol) was added as an oxygen carrier, then catalyst (7.5 g, IR-120) was added into the reactor followed by the addition of hydrogen peroxide drop wise for 30 min. Then the reaction was continued for 10 h at 1000-1100 rpm to ensure the uniform reaction mixture and to avoid the mass transfer limitation. Upon completion of the epoxidation reaction, prior to analysis the samples were washed repeatedly with warm Millipore water (40 °C), until all the catalyst and other reactants were removed to make it neutral. Finally rotary evaporator was used to distilled off solvent and trace water. Epoxidation product was confirmed by \(^1\)H NMR technique, oxirane oxygen content (OOC) analysis. The required physico-chemical properties were estimated for the final epoxide product.

4. Results and discussions

4.1. \(^1\)H NMR spectroscopy

\(^1\)H NMR spectra of CO, COFAME and its epoxide are shown in Figs. 1(a)-1(c). Comparison of CO and its methylesters spectra show that castor oil fatty acid methylesters were prepared by removing high molecular weight glycerol from CO via transesterification reaction. Methyl esters were confirmed by the disappearance of glycerol peak at 4.1 to 4.3 ppm (Fig. 1(a)) and appearance of esters peak at 3.74 ppm (Fig. 1(b)). Similarly, COFAME was epoxidised to synthesise the biolubricant base stock by converting the unsaturation present into oxirane ring. Epoxide product was confirmed by disappearance of double bonds at 5.3 to 5.6 ppm (Fig. 1 (b)) and replaced with the epoxy group of hydrogen peroxide in castor oil methyl esters. The epoxy protons were observed in δ 2.9-3.2 ppm (Fig. 1 (c)) region in the epoxidised castor oil fatty acid methyl esters (epCOFAME). Similar kind of results was noticed by Salimon et al., (2012) during their study on ricinoleic acid epoxidation [11].

4.2. FTIR Spectroscopy

The spectrum from the FTIR analysis exhibits several absorption peaks as shown in Fig. 2. FTIR peaks of COFAME indicates that there is an unsaturation content at 3400 cm\(^{-1}\) (C=C). But, after the epoxidation of COFAME unsaturation peak was disappeared in the same range and an additional peak was appeared in 823-843 cm\(^{-1}\) range. The appearance of epoxy peak at 820-843 cm\(^{-1}\) provided evidence that epoxidation reaction took place using ion-exchange resin as catalyst. Change of functionality in this range indicates that all the unsaturation content was transformed into epoxide product and the same was highlighted in figure 2. Salimon et al. (2012) described that the characteristic signals in the FTIR spectrum of ricinoleic acid at 823-843 cm\(^{-1}\) represent the quaternary carbons of the oxirane ring [12]. The complete disappearance of C=C bonds in the WCO epoxide spectra (Fig. 2) further supported almost complete conversion of double bonds to oxirane (i.e. 98.5%). In this study FTIR spectra exhibited trace of –OH absorption peak at approximately 3000-3500 cm\(^{-1}\) which represents the presence of hydroxyl groups in the COFAME and its epoxide. These hydroxyl groups are belongs to the ricinoleic acid which is the major fatty acid in CO composition.

4.3. physico-chemical characteristics of COFAME and epoxidised castor oil fatty acid methyl esters (epCOFAME)

The main objective behind the epoxidation of COFAME was to modify its structure by eliminating un-saturation content (Indicated by Iodine Value (IV)) into oxirane oxygen ring, there by thermo-oxidative stability of prepared epoxide can be improved. Epoxidized oils can be used as lubricant base fluids due to their good lubricity and higher thermo-oxidative stability compared to its structurally unmodified methyl esters [1]. Because unsaturation content in the oil restricts its direct use as lubricant basestock. Therefore, via epoxidation structure of vegetable oil can be altered to convert un-saturation in oleic, linoleic and linolenic acids into epoxy-groups, thereby improves the thermo-oxidative stability [13]. Lower the IV higher is the thermo-oxidative stability and vice versa. From table 1 it can be seen that for COFAME IV was 84.6 and via epoxidation it was brought down to 1.27. This decreased in IV of COFAME epoxide indicates that almost 98.5% (based on IV) of unsaturation was converted into oxirane ring, which results in improved thermo-oxidative stability (Table 2). The detailed physico-chemical properties of
COFAME and its epoxide are shown in Table 1. Acid value (AV) of COFAME and its epoxide was found to be 1.65 and 1.08 mg KOH/g respectively. Lower acid value of epoxide sample assures that trouble free operation of the equipment on its utilisation. During this study density of epoxidised COFAME (956 kg/m³) was found to be higher than its unmodified COFAME (930 kg/m³). Similarly kinematic viscosity (at 40 °C) of COFAME epoxide (35.81 Cst) was two and half times higher than COFAME (13.61 Cst). This may be due to addition of oxygen molecule in the midst of double bond, thereby increases the intermolecular forces, molecular weight and polarity. From the study it was also observed that epoxidized esters have higher molecular weight and more polar structure than unmodified methyl esters which results in strong interaction between the molecules. This property of epCOFAME enhances the lubricity in dynamic system.

From the Table 1 it was also noticed that the pour point of COFAME epoxide (8 °C) was higher than its unmodified COFAME (-12.5 °C), this can be explained with the help of fatty acid composition of COFAME and detailed description about the same can be found in our earlier findings [10]. The unsaturation content has a positive influence on the pour point i.e. higher the unsaturation content lower the pour point and vice versa. The unsaturated fatty acids content in COFAME (94.6 wt%) was higher than the saturated fatty acid content (3.2), therefore it exhibits lower pour point. But during the epoxidation reaction unsaturation content was converted into oxirane oxygen ring which results in huge difference in the pour point (20.5°C) value. Further, pour point of COFAME epoxide can be improved by additivation or opening of oxirane ring in the presence of alcohols or acids [5, 6]. All together these physicochemical properties have a great significance on the performance of final lubricant base stock and can be used as replacement for conventional hydraulic lube oil.
Fig. 1. CO (a), COFAME (b), COFAME epoxide (c) $^1$H NMR structure.
Table 1. Physico-chemical properties comparison of COFAME, epCOFAME and their characterisation methods.

<table>
<thead>
<tr>
<th>Properties</th>
<th>COFAME</th>
<th>epCOFAME</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Value (mg KOH/g)</td>
<td>1.65</td>
<td>1.08</td>
<td>AOCS (Te 1a-64, 1997)</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>930</td>
<td>956</td>
<td>ASTM D 4052-91</td>
</tr>
<tr>
<td>Iodine Value (gI₂/100g of oil)</td>
<td>84.6</td>
<td>1.27</td>
<td>AOCS (Tg 1-64, 1997)</td>
</tr>
<tr>
<td>Kinematic Viscosity (CSt) at 40 °C</td>
<td>13.61</td>
<td>35.81</td>
<td>ASTM D-445</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-12.5a</td>
<td>8</td>
<td>ASTM D-97</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.94</td>
<td>0.96</td>
<td>ASTM D854-10</td>
</tr>
<tr>
<td>Oxirane Content (Experimental)</td>
<td>-</td>
<td>4.86</td>
<td>AOCS Cd-9, 120</td>
</tr>
<tr>
<td>Oxirane Content (Theoretical)</td>
<td>-</td>
<td>5.06</td>
<td>-</td>
</tr>
<tr>
<td>Relative percentage</td>
<td>-</td>
<td>96.04</td>
<td>-</td>
</tr>
<tr>
<td>Conversion of oxirane (%)</td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a_{Source: 10}\)

### 4.2 Thermo-oxidative stability of COFAME, epCOFAME and conventional hydraulic lubricant base oil

Thermal stability of COFAME, epCOFAME and servo hydraulic lube oil (SHLO) was determined from onset temperatures (OT) of thermal decomposition under nitrogen atmosphere. TG, DTG curves of epCOFAME and SHLO are shown in Figs. 3 and 4. From figures it can be seen that epCOFAME and servo lube oils were thermally stable up to 340 and 260°C respectively. But, beyond the onset temperature decomposition of the samples were noticed. From Table 2 It can be seen that epCOFAME exhibits more thermal stability compared to COFAME and servo hydraulic lube oil (SHLO). Higher thermal stability of epCOFAME was attributed due to the removal of unsaturation content in its fatty acid chain, which improves the thermal stability of epoxide. Alike results were reported by Jin et al., 2008 [14] during their thermal stability study on epoxidised soybean and castor oil. However, in the present study it was observed that conventional SHLO exhibits lower thermal stability compared to epoxidised COFAME. The DTG curves in all the thermograms (Figs. 3 and 4) show that thermal degradation occurred in single continuous step and it involves the breakdown of oxygenated hydrocarbon to lower molecular hydrocarbons, carbon dioxide and carbon monoxide.
Similarly, oxidative stability (oxidative onset temperature) of aforementioned three samples were measured from the oxidative onset temperature under oxygen atmosphere. TG, DTG curves of epCOFAME and SHLO are shown in Figs. 5 and 6. During the analysis single stage degradation pattern was noticed for all the samples. Oxidation onset temperature (OOT) was estimated from respective TG curves and presented in Table 2. From the figures it can be noticed that epCOFAME and servo hydraulic lube oil was stable upto 305 and 250°C (oxidative onset temperature) respectively. But, beyond the onset temperature with gradual increase in temperature considerable weight loss was observed. From the TGA curves of epCOFAME and SHLO it was observed that process of decomposition of SHLO initiated and completed within a temperature range inferior to epCOFAME. The thermo-oxidative stability of epCOFAME (structurally modified ester) was found to be higher compared to COFAME [10]. From this investigation it could be concluded that epCOFAME can act as a potential alternative to conventional hydraulic lubricant. Higher thermo-oxidative stability was ascribed to the removal of unsaturation in the COFAME fatty acid composition. Several authors [15-20] reported that plant oil esters with saturated fatty acids and mono un-saturation content has a positive influence and are thermally and oxidatively more stable than the esters with poly-unsaturation content.

Table 2. Thermo-oxidative stabilities (onset temperatures) of COFAME, epCOFAME and servo hydraulic grade lube oil.

<table>
<thead>
<tr>
<th>Name of the Sample</th>
<th>Onset temperature °C (Under N₂)</th>
<th>Oxidative onset temperature °C (Under O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COFAME</td>
<td>203*</td>
<td>218*</td>
</tr>
<tr>
<td>epCOFAME</td>
<td>340</td>
<td>305</td>
</tr>
<tr>
<td>Servo Hydraulic Lube Oil (SHLO)</td>
<td>260</td>
<td>250</td>
</tr>
</tbody>
</table>

a Source: 10
5. Conclusions

In this study an attempt has been made to prepare bio-lubricant base oil from non-edible renewable raw material like COFAME. In order to utilise methyl esters of castor oil and to enhance the thermo-oxidative stabilities of COFAME, its structure was modified via epoxidation reaction to convert the unsaturated double bonds into oxirane ring. Product was confirmed by $^1$H NMR spectra, oxirane analysis and further significant physico-chemical properties were determined. This work also revealed that, it was possible to estimate the thermo–oxidative stability of the COFAME and its epoxide using thermo gravimetric analysis. It has been also observed that the thermo-oxidative stability of epCOFAME was found to be higher (340, 305 °C) compared to COFAME (203, 218 °C) and SHLO (260, 250 °C). Based on the above outcomes, this study concludes that structurally modified COFAME can be used as potential bio-biolubricant base oil for hydraulic lubricant applications as a replacement to conventional lubricant base oils.

References


