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Thumba (*Citrullus colocynthis* L.) seed oil: a potential bio-lubricant base-stock

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SUMMARY: Thumba seed oil, a minor, renewable tree borne oil, was exploited for the preparation of bio-lubricant base-stocks. The different base-stocks prepared were epoxy thumba oil (ETO), branched, 2-ethylhexyl ester (T2-EtHE), and polyol esters, namely, neopentyl glycol (TNPGE), trimethylolpropane (TTMPE) and pentaerythritol (TPEE) esters of thumba fatty acids. All the base-stocks were thoroughly characterized using spectral techniques. When evaluated for lubricant properties, ETO showed much higher viscosity (216.9 cSt), good oxidative stability (RBOT Method, ASTM D 2272) (20 min) and weld load (ASTM IP 239) (180 kg) behavior when compared to the branched and polyol esters. Polyol esters, T2-EtHE, TNPGE and TTMPE (−9 to −18 °C) showed low pour points compared to ETO and TPEE. The thermal stabilities (Thermo gravimetric analysis, TGA) of ETO and TPEE (425 °C) were higher compared to other base-stocks. The lubricant properties of ETO matched well with ISO VG 220 and Aviation Grade 100 lubricant specifications, while polyol esters can be well exploited for hydraulic and metal working fluid applications.

KEYWORDS: *Epoxidation; Lubricant properties; Polyols; Thumba seed oil*

RESUMEN: ***Aceites de semillas de thumba (*****Citrullus colocynthis*** ***L.): una reserva potencial para biolubricantes***. Las semillas de thumba producen un aceite de escasa importancia que ha sido explotado como base para la preparación de biolubricantes. Los diferentes derivados de thumba preparados fueron: éteres epoxi (ETO), éteres ramificados, éster de 2-etilhexilo (T2-ETHE), y los ésteres de poliol:, neopentil glicol (TNPGE), trimetilolpropano (TTMPE) y pentaeritritol (TPEE). Todas las bases se caracterizaron en su totalidad utilizando técnicas espectrales. Cuando se evaluaron las propiedades del lubricante, ETO mostró una viscosidad mucho más alta (216,9 cSt), buena estabilidad a la oxidación (RBOT Método, ASTM D 2272) (20 min) y buena carga (239 ASTM IP) (180 kg) en comparación con el comportamiento de los ésteres de poliol y los ramificados. Los ésteres de poliol, T2-EEl, TNPGE y TTMPE (−9 a −18 °C) mostraron bajos puntos de fluidez en comparación con ETO y TPE. Las estabilidades térmicas (análisis termogravimétrico, TGA) de ETO y TPE (425 °C) fueron más altos en comparación con las otras bases. Las propiedades lubricantes de ETO coinciden bien con las especificaciones de los lubricantes, ISO VG 220 y Grado Aeronautica 100, mientras que los ésteres de poliol pueden aprovecharse bien para aplicaciones en fluidos hidráulicos y trabajos de metal.

PALABRAS CLAVE: *Aceite de semilla de Thumba; Epoxidación; Polioles; Propiedades de los lubricantes*

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1. INTRODUCTION

The use of renewable resources in industrial applications has been of interest in the governmental (Hagstrom, 2005), commercial (Tullo, 2007) and, more importantly, consumer conscience (Guzman, 2004; Arnum 2005; Walmart, 2006). During the past few years the importance of environmentally friendly lubricants has been increasing (Rhee, 1996) rapidly. Vegetable oils form the renewable feed stocks for most industrial applications and are in greater demand in critical areas requiring "total loss" or "once through" materials like two-cycle-engine oils, chain saw lubricants, hydraulic fluids, boat engines, tractors, agricultural equipment, metal working fluids, refrigeration oils, and so on (Ademezewska and Wilson, 1997; Pavlovicova and Cvengros, 1999; Erhan and Asadauskas, 2000). Many global initiatives have been undertaken to increase the market share of environmentally friendly bio-based lubricants. Vegetable oil based lubricants are natural, renewable, less toxic and easily biodegradable. In addition, they have a superior viscosity index, lubricity characteristics and solubilizing power for polar contaminants and additive molecules (Ademezewska and Wilson, 1997; Pavlovicova and Cvengros, 1999; Erhan and Asadauskas, 2000; Erhan *et al.*, 2006). They show a much lower coefficient of friction, which can lead to reduced energy consumption for almost any part of the equipment in which they are used.

However, vegetable oils suffer from poor oxidative and thermal stabilities, which is due to the high degree of unsaturation in the fatty acid chain of the olefin and β- hydrogen of glycerol backbone which are susceptible to oxidation (Gapinski *et al.*, 1994). Therefore, improving the oxidative stability and thermal stability is important in maintaining their sustainability and performance as lubricants. Chemical modifications at unsaturation like epoxidation, hydroxylation, acylation etc., are some of the methods that can improve the performance of the base-stocks (Wu *et al.*, 2000; Hwang and Erhan, 2001; Adhvaryu and Erhan, 2002; Adhvaryu *et al.*, 2005; Harry-O'kuru *et al.*, 2011). Also the epoxy vegetable oils have several applications like lubricating additives to eliminate corrosion from chlorine containing compounds (Tao *et al.*, 1996) as used in metal working fluids and high-temperature lubricants (Randles and Wright 1992; Wu *et al.*, 2000) and the products obtained from ring opening can be employed as low-temperature lubricants (Lathi and Mattiasson, 2000).

Epoxidation of the double bond is a common reaction, where the double bond is converted into an oxirane ring in the presence of a suitable oxidizing reagent. The most common epoxidation process is carried out using peracetic or performic acid, with soluble mineral acids like sulphuric acid as catalyst. But traditionally employed low cost mineral acids often hinder the achievement of high yields owing to the oxirane ring opening leading to deleterious consecutive reactions (Rangarajan *et al.*, 1995; Asadauskas and Erhan, 1999; Petrovic *et al.*, 2002). The environmental concerns related to the disposal of salts during the neutralization of mineral acids and the technical problems associated with their use such as corrosion and separation constitute a strong driving force in searching for alternatives to this technology. In this context, few researchers have employed heterogeneous catalysts (Tanabe and Hoelderich, 1999; Hoelderich, 2000) and acidic ion exchange resins to synthesize epoxides (Goud *et al.*, 2007) which are not economically and industrially feasible. However, it is important to protect the environment through green processes. Hence, in the present study, a mineral acid free process was employed to prepare the epoxy thumba oil.

The presence of a β- hydrogen atom in the triglyceride is susceptible to oxidation resulting in partial fragmentation of the molecule and the fragmented unsaturated molecules undergo polymerization and result in the formation of precipitate particles (Gapinski, 1994). The esterification of vegetable oils with polyols and branched chain alcohols (Bünemann *et al.*, 2000), overcomes the above disadvantage. The esterification of fatty acids or transesterification of fatty acid methyl esters with polyols like trimethylolpropane (TMP) or neopentyl glycol (NPG) have been developed for preparing a variety of lubricating oils (Chang *et al.*, 2012; Padmaja *et al.*, 2012). It was observed that the polyol esters exhibited good viscosity indices and lower pour points (−18 °C to −3 °C). 2-Ethylhexyl esters are widely used as coolants and lubricants for the machinization of metals and for drilling oils (Berthezene *et al.*, 1999; May *et al.*, 2005; Herrmann *et al.*, 2007) and Asadauskus and Erhan (Asadauskas and Erhan, 1999) used such esters to improve the pour point properties of the bio-lubricant, and for allowing their use as additives.

The economics of the process also depends on the selection of raw materials. A wide variety of edible oils were employed in the preparation of bio-lubricants through epoxidation and other modifications; the most common being soybean oil (Hwang and Erhan, 2001; Adhvaryu and Erhan, 2002) and rapeseed oil (Wu *et al.*, 2000). In a country like India, which imports huge quantities of edible oils (10.3 million tons, 2012) annually, cannot afford to use common edible oils for non-edible applications. Thumba seed oil is consumed in a few tribal areas, but has not been fully exploited. Therefore, the present study was focused on the use of the minor tree-borne thumba (*Citrullus colocynthis* L.) oil for the preparation of bio-lubricant base-stocks. Though there are reports on the utilization of thumba seed oil for bio-diesel preparation (Shiv Lal *et al.*, 2011), there are no studies on the use of this oil as a potential lubricant base-stock. Hence, an attempt was made to prepare epoxy thumba oil (ETO) and branched and polyol esters of thumba fatty acids namely 2-ethylhexyl, NPG, TMP and pentaerythritol (PE) esters. These base-stocks were evaluated for lubricant properties and the properties which were compared with different lubricant specifications. These studies may further help in finding alternatives to petroleum-based products.

The plant is highly xerophytic and grows wild in the semi-deserts and deserts of North Africa, Afghanistan, Baluchistan, Iran, Arab, Spain, Portugal, Japan and India. In India they are widely grown in arid and semi-arid regions of Haryana, Rajasthan, Gujarat, Madhya Pradesh and Uttar Pradesh (www.crirec.com). It is a creeper and flourishes in any environment as it grows rapidly, requiring no attention once the seeds are sown. Hence developing high value products from thumba seed oil will help to boost the economy of the farmers, tribal farmers in particular.

2. MATERIALS AND METHODS

2.1. Materials

Thumba seeds were procured from the M/s. Sanjeevani Herbal Health Society, Hyderabad. Hydrogen peroxide (H_2O_2), formic acid (HCOOH), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), 4 N hydrobromic acid (HBr), iodine monochloride (ICl), potassium hydroxide (KOH), hydrochloric acid (HCl), n-butanol, pyridine, chloroform, acetic anhydride, 2-EtH, NPG, TMP, PE, p-TSA, xylene, aluminium oxide active basic, sodium hydroxide (NaOH) and sodium sulphate were procured from M/s S.D. Fine chemicals Pvt. Ltd., Mumbai, India. All the solvents and reagents were of analytical grade and used directly without purification.

2.2. Gas Chromatographic analysis

The fatty acid composition of the oil was analyzed using a gas chromatography by taking fatty acid methyl esters. Epoxy thumba methyl esters were prepared by the transesterification of epoxy thumba oil. A mixture of epoxy thumba oil (5.0 g) and sodium methoxide (0.05 g, wt% of substrate) dissolved in 15 mL methanol was stirred magnetically at 60–65 °C. The formation of methyl esters was monitored by TLC using the solvent system n-hexane/ethyl acetate (90:10 v/v). After completion of the reaction, the solvent was removed using a rotary evaporator, and the contents were extracted with ethyl acetate, and washed with water until neutralization. The organic phase was passed through sodium sulphate, concentrated and dried under reduced pressure (2–5 mm Hg) to afford epoxy thumba fatty acid methyl esters (yield 4.7 g, 96%).

GC analysis of the methyl ester was carried out using the GC 6890 N series of Agilent and an HP 1 column (i.d. 0.25 mm, length 30 m). The injector and flame ionization detector were at 300 °C. The oven temperature was programmed at 150 °C for 2 min and then increased to 300 °C at 8 $°C \cdot min^{-1}$. The carrier gas used was nitrogen at a flow rate of 1.5 $mL \cdot min^{-1}$. The GC-MS analyses were recorded using an Agilent 6890N gas chromatograph with an HP-1 MS capillary column (30 m × 0.25 mm × 0.5 μm) connected to an Agilent 5973 mass spectrometer at 70 eV (*m/z* 50-600; source at 230 °C and quadrupole at 150 °C) in the EI mode.

2.3. Spectral analysis

Infrared (IR) spectra were obtained on a 1600 FT-IR Perkin-Elmer Spectrometer (Norwalk, CT) with a liquid film between the NaCl cells. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded in $CDCl_3$ on an Avance 300 MHz spectrometer. Chemical shifts relative to TMS as internal standard are given as δ values in ppm. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in $CDCl_3$ on a Varian (75 MHz) spectrometer. Mass spectra were recorded by electrospray ionization (ESI) on a Shimadzu LC/MS instrument.

2.4. Thermo-gravimetric analysis (TGA)

TGA studies were carried out in a non-isothermal mode employing a Mettler Toledo TGA instrument to get the decomposition pattern of the base-stocks. About 5 mg of the sample were taken in an aluminum crucible and heated slowly up to 600 °C at a rate of 10 $°C \cdot min^{-1}$ under nitrogen atmosphere to get the TGA onset temperature.

2.5. Physico-chemical and lubricant properties

The physico-chemical analyses of thumba seed oil and its derivatives (base-stocks) was carried out using standard AOCS and ASTM methods namely acid value, AOCS, 2009; iodine value, AOCS, 2003a; saponification value, AOCS, 2003b; unsaponifiable matter, AOCS, 2003c; oxirane value, AOCS, 1997a, hydroxyl value, AOCS, 1997b and peroxide value, IUPAC 2.421 (Paquot and Hautfenne,1987).

The lubricant properties were determined using the standard AOCS and ASTM methods and the details are as follows:

Density. The density of the products was determined using an Anton Paar DMA 4500 M density meter at 15 °C as per the ASTM method (ASTM, 2011). The measurements were carried out thrice and the results reported are an average of the three.

Kinematic viscosity and viscosity index (*VI*). Kinematic viscosity was measured using calibrated Cannon Fenske viscometer tubes in a Cannon

Constant Temperature Viscosity Bath (Cannon Instrument Co., U.S.A.) at 40 °C and 100 °C. Viscosity and viscosity index (VI) were calculated using ASTM D 445 (ASTM, 1998) and ASTM D 2270 (ASTM, 2002a) methods, respectively. Duplicate measurements were made and the average values are reported.

Kinematic Viscosity (cSt) = Viscometer constant (cSt/s) × time (s)

Pour point. The pour points of the products were determined according to the ASTM D 97 method (ASTM, 2005) with an accuracy of ± 3 °C using the pour point test apparatus manufactured by Dott Scavini & Co, Italy. The sample temperature was measured in 3 °C increments at the top of the sample until it stopped pouring, and all the runs were carried out in duplicate.

Flash point. The Flash points of the products were determined using the Tanaka Scientific Ltd., Japan, apparatus according to the ASTM D 93 method (ASTM, 2002b). Duplicate measurements were made and the average values are reported.

Copper corrosion. The determination of corrosiveness of the products was done using the Koehler Inc., U.S.A. apparatus as per the ASTM D 130 method (ASTM, 2004). A polished Cu strip is immersed in 30 mL of the sample being tested at 100 °C for 3 h. After 3 h, the Cu strip is removed, washed with n-hexane, and the color and tarnish level were assessed against the ASTM Copper Strip Corrosion Standard.

Oxidative stability by rotating bomb oxidation test (*RBOT*). The oxidative stability of the products was measured using a Koehler Inc., U.S.A. Rotator Bomb Oxidation Test apparatus as per the ASTM D 2272 test method (ASTM, 2002a). The experiment was carried out at 150 °C, with a Cu catalyst, 55.5 g; sample, 50 g and water, 5 mL. The vessel was sealed and charged with oxygen to 90 psi pressure. The test was completed once the pressure dropped more than 25 psi below the maximum pressure.

Weld load. The weld load of the products was determined using the Four Ball Tester manufactured by Stanhope Seta, U.K. according to the ASTM IP 239 method (ASTM, 2002c). Out of four balls, three clean balls are placed in the ball cup securely and the fourth ball is placed into the upper ball chuck. The ball cup assembly is positioned centrally under the spindle in contact with the fourth ball. Then the series of loads are applied on the weight pan with an increment of 10 kg and the motor is started for a period of 1 minute. The load at which the balls are welded or fused together is taken as the Weld load of the product.

Wear. The wear of the products was determined using the Four Ball Tester manufactured by Stanhope Seta, U.K. as per the ASTM D 4172 method (ASTM, 2002d). The point contact interface is obtained by rotating a 12.7mm diameter steel ball under load against three stationary steel balls immersed in the lubricant. To evaluate the anti-wear characteristics of lubricants, the subsequent wear scar diameters on the balls is measured.

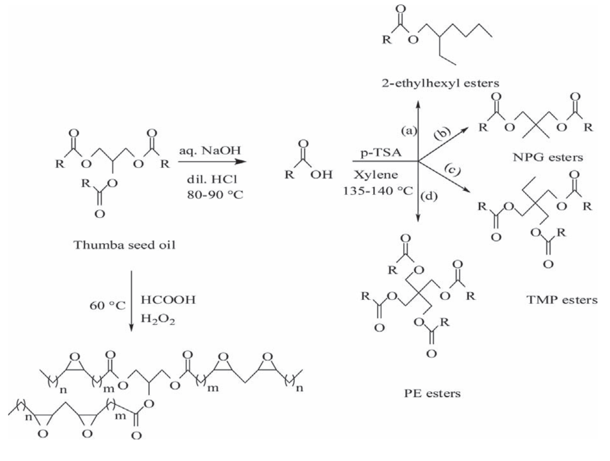
2.6. Extraction of thumba seed oil

Thumba seed oil (190 g, 19%) was obtained by the soxhlet extraction of thumba seeds (1000 g) employing the procedure described in our earlier work (Kamalakar *et al*., 2013).

2.7. Synthesis of epoxy thumba seed oil and of thumba fatty acids and their branched and polyol esters

2.7.1. Epoxidation of thumba seed oil

Epoxidation was carried out by varying the molar ratios of formic acid (2–3.5 mol) and hydrogen peroxide (4–8 mol). The general reaction for the epoxidation is shown in Scheme 1. In a typical optimized experiment, thumba oil (30 g, 0.034 mol) was placed in a three necked 250 mL round bottomed flask, equipped with a mechanical stirrer, a condenser and a thermometer immersed in a thermostatic water bath whose temperature could be controlled within ± 2 °C. A calculated amount of formic acid (3.94 mL, 0.102 mol) was charged into the flask and the mixture was stirred for 10–15 min. This was followed by the addition of a calculated amount of 30% aq hydrogen peroxide (17.35 mL, 0.17 mol) using a dropping funnel, maintaining the temperature at 5–10 °C. This precaution was taken to prevent over heating of the system due to the exothermic nature of the epoxidation. Then the temperature was slowly raised to 60 °C and the reaction continued for 7 h. The course of the reaction was monitored by withdrawing aliquots of the reaction mixture at various time intervals. The samples were extracted with



SCHEME 1. Preparation of epoxy thumba oil and 2-ethylhexyl, NPG, TMP and PE esters of thumba fatty acids

ethyl acetate, washed with water until they were acid free, and analyzed for their oxirane value. The maximum epoxidized thumba oil was analyzed for iodine value and subjected to GC analysis. The structure of epoxy thumba oil was characterized by IR, ^{1}H NMR, ^{13}C NMR and ESI-MS spectral studies.

After completion of the reaction, the solvent was removed using a rotary evaporator, and the contents were extracted with ethyl acetate, and washed with water until neutralization. The organic phase was passed through sodium sulphate, concentrated and dried under reduced pressure (2–5 mm Hg) to afford epoxy thumba seed oil. Epoxy thumba seed oil methyl esters were prepared, and analyzed by GC (Table 1) and GC-MS.

GC-MS (*EI, 70eV*). Epoxy 18:0: 55, 74, 83, 155, 199, 281, 312 (M+.), Epoxy 18:1: 81, 155, 164, 207, 235, 297, 310 (M+.) and diepoxy 18:0: 55, 81, 155, 187, 211, 237, 277, 295, 326 (M+.).

IR (*neat, cm*$^{-1}$). 1743.77 (-C=O); 1162.43 (C-O-C(O)-); 824.61 (epoxy ring).

^{1}*H NMR* (*CDCl*$_3$, *δ ppm*). 0.86-0.93 (m, 9H, -CH$_2$-CH$_3$); 1.25-1.33 (m, -(CH$_2$)$_n$-); 1.49-1.52 (m, CH$_2$-CHOCH-); 1.63 (m, 6H, -CH$_2$-CH$_2$-C(O)-O); 1.73 (t, -CHOCH-CH$_2$-CHOCH-) 2.30 (t, 6H, -CH$_2$-C(O)-O); 2.90-3.15 (m,-CHOCH-); 4.10-4.32 (dd, 4H, OCH$_2$-CH); 5.27 (qt, 1H, OCH-(CH$_2$)$_2$).

^{13}*C NMR* (*CDCl*$_3$, *δ ppm*). 13.9-14.1 (CH$_3$-CH$_2$-); 22.5-32.5 (-CH$_2$-); 34.0 (-CH$_2$-C(O)-O-C); 54.1-57.2 (-CHOCH-); 62.0 (-CH$_2$-O-C(O)-); 68.8 (-CHO-C(O)-); 129.8 (-CH=CH-), 172.7-173.2 (-C(O)-).

ESI-MS (*m/z*). 914 (POO diepoxy+Na$^+$); 926 (SSL monoepoxy+Na$^+$); 942 (SSL/SOO diepoxy+Na$^+$); 968 (OOL tetraepoxy+Na$^+$); 970 (OOL tetraepoxy+Na$^+$); 982 (LLL penta epoxy+Na$^+$); 984 (OLL penta epoxy+Na$^+$); 998 (LLL hexaepoxy+Na$^+$).

2.7.2. Typical procedure for the preparation of thumba fatty acids

Thumba oil (300 g, 0.34 mol) and a sodium hydroxide solution (54 g, 1.35 mol, in 675 mL water) were stirred mechanically for 4 h at 80–90 °C. After 4 h, the reaction mixture was cooled to 50 °C, acidified to ~pH 5 with dilute hydrochloric acid and the contents were extracted with ethyl acetate, washed with water to remove the excess of HCl, followed by drying over anhydrous sodium sulphate. The sample was concentrated using a rotary evaporator and dried under reduced pressure (2–5 mm Hg) to obtain 279 g (98% yield) of thumba fatty acids.

TABLE 1. Fatty acid composition of thumba and epoxy thumba fatty acid methyl esters

Fatty Acid	Composition (wt%) of TO	Composition (wt%) of ETO
Palmitic (16:0)	10.3	10.5
Stearic (18:0)	8.0	8.5
Oleic (18:1)	24.5	–
Linoleic (18:2)	55.9	–
Epoxy (18:0)	–	25.1
epoxy (18:1)	–	4.3
diepoxy (18:0)	–	50.1
Arachidic (20:0)	0.4	0.5
Others	0.9	1.0

2.7.3. A typical procedure for the preparation of 2-ethylhexyl esters of thumba fatty acids (T2-EtHE)

The general reaction for the esterification of thumba fatty acids is shown in Scheme 1. 2-Ethylhexanol (209.7 g, 1.61 mol), thumba fatty acids (300 g, 1.075 mol) and xylene (100 mL) were colloected in a three necked reaction flask equipped with a thermometer, condenser and a Dean Stark apparatus. The reaction mixture was stirred at 135–140 °C in the presence of p-TSA (3.0 g, wt% based on fatty acid mixture) as catalyst until a theoretical amount of water (19.3 mL) was collected. The product was distilled at 130–140 °C under the reduced pressure of 2–3 mm Hg to remove xylene and unreacted 2-ethyl hexanol. The reaction mixture was extracted with ethyl acetate, washed with water and passed over anhydrous sodium sulphate, concentrated using a rotary evaporator and dried under reduced pressure. The contents were then passed through a basic alumina column chromatography to remove unreacted fatty acids. The product (T2-EtHE) obtained was 399.6 g (97% yield) and the ester was analyzed for acid and hydroxyl values. The structure of T2-EtHE was characterized by IR, ^{1}H NMR, ^{13}C NMR, ESI-MS and GC-MS spectral studies.

IR (*neat, cm*$^{-1}$). 3010.26 (=C-H); 1736.92 (-C=O); 1181.26 (C-O).

^{1}*HNMR* (*CDCl*$_3$, *δ ppm*). 0.89 (m, 9H, -CH$_2$-CH$_3$); 1.25-1.4 (m, -(CH$_2$)$_n$); 1.52-1.67 (m, 2H, -CH$_2$-CH$_2$-CH$_2$-C(O)-O); 1.97-2.05 (m,-CH-CH$_2$-CO-, -CH=CH-CH$_2$-); 2.3 (t, 2H, -CH$_2$-CH$_2$-C(O)-O-); 2.42 (m, -CH$_2$-CH=CH-CH$_2$-CH=CH-); 4.0 (d, 2H, -CH-CH$_2$-O-C(O)-); 5.32-5.36 (m, -CH$_2$-CH=CH-CH$_2$-).

^{13}*CNMR* (*CDCl*$_3$, *δ ppm*). 10.9 (CH$_3$-CH$_2$-CH-); 14.0 (-CH$_3$); 22.5-31.9 (-(CH$_2$)$_n$-); 34.4 (-HC=HC-CH$_2$-CH=CH-); 38.7 (-C(O)-O-CH$_2$-CH-); 66.6 (-C(O)-O-CH$_2$-CH-); 127.7 (-CH=CH-CH$_2$-CH=CH-); 129.7 (-CH=CH-CH$_2$-CH=CH-); 174.0 (-C(O)-).

2.7.4. A typical procedure for the preparation of NPG esters of thumba fatty acids (TNPGE)

NPG (44.73 g, 0.43 mol), thumba fatty acids (300 g, 1.075 mol) and xylene (100 mL) were collected in a three necked reaction flask equipped with a thermometer, condenser and a Dean Stark apparatus. The reaction mixture was stirred at 135–140 °C in the presence of p-TSA (3.0 g, wt% based on fatty acid mixture) as catalyst until the theoretical amount of water (15.4 mL) was collected. The product was distilled at 110–115 °C under a reduced pressure of 2–3 mm Hg to remove xylene. The reaction mixture was extracted with ethyl acetate, washed with water, passed over anhydrous sodium sulfate, and concentrated using a rotary evaporator, and dried under reduced pressure. The residue, subjected to basic alumina column chromatography to remove unreacted fatty acids, afforded 255.7 g of the product (95% yield). The ester was analyzed for acid value and hydroxyl value.

A similar procedure was followed for the preparation of the TMP esters of thumba fatty acids (TTMPE) and the PE esters of thumba fatty acids (TPEE) taking TMP (41.13 g, 0.307 mol) and PE (32.36 g, 0.238 mol) respectively. The yields were found to be 260 g (92.5%) for TTMPE and 247.2 g (89%) for TPEE. The structures of TNPGE, TTMPE and TPEE were characterized by IR, ^{1}H NMR, ^{13}C NMR and ESI-MS spectral studies.

NPG esters of thumba fatty acids (TNPGE)

IR (*neat, cm*$^{-1}$). 3009.73 (=C-H); 1741.70 (-C=O); 1164.36 (C-O).

^{1}*H NMR* (*CDCl*$_3$, *δ ppm*). 0.88 (t, 6H, -CH$_2$-CH$_3$); 0.96 (s, 6H, -C-CH$_3$); 1.2-1.40 (m, -(CH$_2$)$_n$); 1.58-1.61(m, 4H, -CO-CH$_2$-CH$_2$-CH$_2$-); 1.97-2.04(m, -CH$_2$-CH=CH-CH$_2$-); 2.3(t, 4H, -CH$_2$-CH$_2$-C(O)-O-); 2.75-2.8 (m, -HC=HC-CH$_2$-CH=CH-); 3.78 (s, 4H, -C-CH$_2$-O-C(O)-); 5.3-5.4 (m, -CH=CH-CH$_2$-).

^{13}*C NMR* (*CDCl*$_3$, *δ ppm*). 14.03 (-CH$_3$); 22.6 (CH$_3$-C- CH$_3$); 24.9 (CH$_3$-CH$_2$-); 25.6 (-CO- CH$_2$-CH$_2$-); 27.1-29.6 (-(CH$_2$)$_n$-); 31.45-31.8(-CH$_2$-HC=HC-CH$_2$-CH=CH-CH$_2$-); 34.14(-CO-CH$_2$-); 40.6 (-HC=HC-CH$_2$-CH=CH-); 69.0 (-CO-O-CH$_2$-CH-); 127.8 (-CH=CH-CH$_2$-CH=CH-); 129.9 (-CH=CH-CH$_2$-CH=CH-); 173. 6 (-CO-).

TMP esters of thumba fatty acids (TTMPE)

IR (*neat, cm*$^{-1}$). 3009.81 (=C-H); 1742.93 (-C=O); 1168.00 (C-O).

^{1}*HNMR* (*CDCl*$_3$, *ppm*). 0.88 (t, 9H, -CH$_2$-CH$_3$); 1.25-1.3 (m, (-CH$_2$-)$_n$); 1.44-1.52 (q, 2H, -C-CH$_2$-CH$_3$); 1.56-1.65 (m, 6H, -O-C(O)-CH$_2$-CH$_2$-CH$_2$-); 1.98-2.08 (m, -CH$_2$-CH$_2$-CH=CH-); 2.28-2.33 (t, 6H, -O-C(O)-CH$_2$-CH$_2$-); 2.75-2.79 (t, -CH=CH-CH$_2$-CH=CH-); 4.0 (S, 6H, -C-CH$_2$-O-C(O)-R); 5.29-5.4 (m, -CH$_2$-CH=CH-CH$_2$-).

^{13}*C NMR* (*CDCl*$_3$, *ppm*). 7.3 (CH$_3$-CH$_2$-C-); 14.03 (-CH$_3$); 22.62 (CH$_3$-CH$_2$-C-); 24.87 (CH$_3$-CH$_2$-); 25.6 (-O-C(O)-CH$_2$-CH$_2$-); 27.13-29.64 (-(CH$_2$)$_n$-); 31.45-31.8 (-CH$_2$-HC=HC-CH$_2$-CH=CH—CH$_2$-); 34.14 (-O-C(O)-CH$_2$-); 40.58 (-HC=HC-CH$_2$-CH=CH-); 63.65 (-C(O)-O-CH$_2$-CH-); 128 (-CH=CH-CH$_2$-CH=CH-); 129.9 (-CH=CH-CH$_2$-CH=CH-); 173.36 (-C(O)-).

PE esters of thumba fatty acids (TPEE)

IR (*neat, cm*$^{-1}$). 3008.37 (=C-H); 1747.24 (-C=O); 1163.74 (C-O).

^{1}*HNMR* (*CDCl*$_3$, *ppm*). 0.98 (t, 12H, -CH$_2$-CH$_3$); 1.25-1.28 (m, (-CH$_2$-)$_n$); 1.6 (m, 8H, -O-C(O)-CH$_2$-CH$_2$-CH$_2$-); 1.98-2.13 (m, -CH$_2$-CH$_2$-CH=CH-); 2.3 (t, 8H, -O-C(O)-CH$_2$-CH$_2$-); 2.79 (t, -CH=CH-CH$_2$-CH=CH-); 4.11 (S, 8H, -C-CH$_2$-O-C(O)-R); 5.28-5.43 (m, -CH$_2$-CH=CH-CH$_2$-).

^{13}*C NMR* (*CDCl*$_3$, *ppm*). 14.0 (CH$_3$); 22.6 (CH$_3$-CH$_2$-); 25.5 (-O-C(O)-CH$_2$-CH$_2$-); 27.1-29.6 (-(CH$_2$)$_n$-); 31.5-31.8 (-CH$_2$-HC=HC-CH$_2$-CH=CH—CH$_2$-); 34.0 (-O-CO-CH$_2$-); 41.8 (-HC=HC-CH$_2$-CH=CH-); 62.0 (-C(O)-O-CH$_2$-CH-); 128 (-CH=CH-CH$_2$-CH=CH-); 129.9 (-CH=CH-CH$_2$-CH=CH-).

3. RESULTS AND DISCUSSION

Most of the epoxy bio-lubricant base-stocks reported in the literature came from common edible sources like rapeseed and soybean oils (Wu *et al.*, 2000; Adhvaryu and Erhan, 2002). The present study is focused on the use of a minor thumba seed oil, rich in unsaturation (80.9%), growing wild in India, for the preparation of lubricant base-stocks. The soxhlet extracted oil was found to be a yellow colored liquid with a viscosity of 36.9 cSt at 40 °C. The physico-chemical properties of the oil are shown in Table 2. The oil was epoxidized at the double bonds to prepare epoxy thumba oil under mineral acid free conditions. Branching and reaction with polyols further improves some of the properties of lubricant base-stocks (Daniel *et al.*, 2011). Therefore, thumba oil was hydrolyzed to fatty acids and reacted with 2-EtH, NPG, TMP and PE to prepare corresponding T2-EtHE, TNPGE, TTMPE and TPEE esters.

3.1. Epoxy thumba seed oil

The epoxidation of thumba seed oil was optimized by varying, initially, the proportion of formic acid from 2.0–3.5 mol, maintaining the amount of H$_2$O$_2$ (5 mol), constant at 60 °C. It was observed that as the concentration of formic acid increased, the oxirane value increased. Maximum oxirane value (6.44) was observed at 7 h when 3 mol of formic acid were used. The reaction was then optimized with respect to the concentration of H$_2$O$_2$, varying from 4-8 mol, keeping the concentration of formic acid (3 mol) constant at 60 °C. A maximum oxirane value of 6.44 was achieved with 5.0 mol of H$_2$O$_2$ at 7 h. Therefore, the optimum condition for the maximum epoxidation of thumba seed oil was 3 mol of HCOOH and 5 mol of H$_2$O$_2$ at 60 °C for 7 h.

TABLE 2. Physico-chemical properties of thumba seed oil

Property	Method	Value
Acid value (mgKOH·g^{-1})	AOCS Cd 3d-63	2.2
Iodine value (g·100g^{-1})	AOCS Cd 1-25	126.4
Peroxide value	IUPAC 2.421	0.1
Saponification value	AOCS Cd 3-25	189.7
Unsaponifiable matter (wt%)	AOCS Ja 6a-40	2.25
Viscosity (cSt) at 40 °C	ASTM D 445	36.9

The epoxidation under the above condition was found to be better compared to the process employing sulphuric acid, as used in most of the epoxidation reactions (Okieimen *et al.*, 2002).

The structure of ETO was confirmed using GC, GC-MS, IR, ^{1}H NMR, ^{13}C NMR and ESI-MS spectral studies. The gas chromatography analysis of ETO showed the presence of C18:0 epoxy group (25.1%) obtained from oleic acid and C18:1 monoepoxy (4.3%) and C18:0 diepoxy (50.1%) groups obtained from linoleic acid. The gas chromatographic data indicated that nearly the entire C=C unsaturation in thumba seed oil had been converted to the epoxy group. The presence of epoxy stretching at 824.61 cm^{-1} as observed in the IR spectra revealed the formation of an epoxy ring. The presence of a multiplet at δ 2.90-3.15 in ^{1}H NMR further confirmed it. In ^{13}C NMR, characteristic peaks were observed at δ 54.1–57.2. ESI-MS also showed the expected molecular ion peaks.

3.2. Branched mono, T2-EtHE and polyol, TNPGE, TTMPE and TPEE esters

The branched and polyol esters were prepared following the procedure employed in our previous study on rubber fatty acid based lubricant base-stocks (Kamalakar *et al.*, 2013). The structures of T2-EtHE, TNPGE, TTMPE and TPEE were confirmed using IR, ^{1}H NMR, ^{13}C NMR and ESI-MS spectral studies. The low hydroxyl values of the polyol esters (≤4.7) confirmed complete esterification.

3.3. Lubricant properties of ETO, T2-EtHE, TNPGE, TTMPE and TPEE

The lubricant properties of ETO, T2-EtHE, TNPGE, TTMPE and TPEE are shown in Tables 3 and 4. ETO exhibited much higher viscosities (216.9 cSt at 40 °C; 22.7 cSt at 100 °C) compared to reported epoxy rapeseed and soybean oils (Wu *et al.*, 2000; Adhvaryu and Erhan, 2002). This could be due to the presence of higher percentage of epoxy content. ETO with good (128) viscosity index (VI) falls under the group III category of base fluids according to the API classification with their VI values well above 120.

Polyol esters based on their viscosities can be categorized to viscosity grades, ISO VG 7, ISO VG 22, ISO VG 46, or ISO VG 68 base-stocks and they can be used in hydraulic fluid applications according to the requirements of ISO 15380 specifications (Paeglis, *et al.*, 2009). Among the polyol esters, the high viscosity of PE esters is due to a higher number of acyl groups. The polyol esters with high VI (189–220) can be exploited for a number of automobile engine, automotive and industrial hydraulic fluid applications (Booser, 1984).

The pour points of the branched and polyol esters of thumba fatty acids were lower compared to ETO, which could be due to the more effective disruption of molecular packing in the former. Hence these can be exploited for hydraulic and metal working fluid applications (Booser, 1984). The pour point of the epoxy oil (−3 °C) was found higher when compared to reported ERO and soybean oils (Wu *et al.*, 2000; Adhvaryu and Erhan, 2002), the most common bio-lubricant base-stocks. However, the pour point can be further reduced by using appropriate pour point depressants and diluents (Asadauskas and Erhan, 1999).

The ETO and polyol esters of thumba fatty acids exhibited high flash points (226–318 °C). Among these, TPEE exhibited a very high flash point, followed by ETO and TTMPE. Hence, these base-stocks can be exploited for high temperature applications (Randles and Wright, 1992; Wu *et al.*, 2000). All the base-stocks with a flash point ≥165 °C lie well within the range of hydraulic oils (Paeglis *et al.*, 2009). Corrosiveness was found to be very good for all the products (1a).

ETO exhibited a good oxidative stability of 20 min, which is stable compared to the polyol esters, T2-EtHE (12 min), TNPGE (15min), TTMPE (12 min) and TPEE (10 min). The stability was also found comparable to other reported base-stocks (Mckeon *et al.*, 2007; Padmaja *et al.*, 2012; Kamalakar *et al.*, 2013). All the base-stocks exhibited high thermal stabilities as indicated by the TGA onset temperature, i.e., 305–465 °C. The TGA degradation onset temperature, which indicates resistance to thermal degradation, was found to be higher in the case of TPEE (425 °C) and ETO (425 °C) followed by TTMPE (405 °C), TNPGE (350 °C) and T2-EtHE (247 °C). The thermal stabilities of the thumba polyol base-stocks were found to be higher compared to UDA-based polyol esters (Padmaja *et al.*, 2012). The ETO with its high viscosity, and good oxidative and thermal stabilities can be well exploited for Aviation Grade 100 lubricant applications, which require stringent specifications (Booser, 1984).

Weld load behavior, which is an important factor that determines the load-carrying capacity

Table 3. Physico-chemical and lubricant properties of epoxy thumba oil (ETO)

Test		Method	ETO	ERO	AG 100
Acid value (mgKOH·g^{-1})		AOCS Cd 3d-63	0.423	0.653	–
Oxirane value (%)		AOCS Cd 9-57	6.44	4.9	–
Iodine value (g·100 g^{-1})		AOCS Cd 1-25	4.5	4.1	–
Density at 15 °C		ASTM D-4052	0.98593	0.9615	–
Specific gravity at 15 °C		ASTM D-4052	0.99367	–	–
Kinematic viscosity (cSt) at	40 °C	ASTM D 445	216.9	86.7	216
	100 °C		22.7	12.7	19.6
Viscosity index (VI)		ASTM D 2270	128	145	103
Pour point (°C)		ASTM D 97	−3	−12	−18
Flash point (°C)		ASTM D 93	289	239	244
Copper corrosion		ASTM D 130	1a	–	–
Oxidative stability (min) (RBOT)		ASTM D 2272	20	–	–
TGA onset temperature			425	–	–
Weld load (kg)		ASTM IP 239	180	70	–
Wear (mm)		ASTM D 4172	0.81	0.71	–

Table 4. Physico-chemical and lubricant properties of T2-EtHE, TNPGE, TTMPE and TPEE

Test		Method	T2-EtHE	TNPGE	TTMPE	TPEE
Acid value (mgKOH·g^{-1})		AOCS Cd 3d-63	0.196	0.137	0.213	0.367
Hydroxyl value (mgKOH·g^{-1})		AOCS Cd 13-60	–	1.82	2.8	4.68
Density at 15 °C		ASTM D-4052	0.87327	0.90640	0.92393	0.93014
Specific gravity at 15 °C		ASTM D-4052	0.87406	0.90721	0.92476	0.93098
Kinematic viscosity (cSt) at	40 °C	ASTM D 445	7.55	20.65	38.86	60.26
	100 °C		2.53	5.45	8.60	11.89
Viscosity index (VI)		ASTM D 2270	189	220	209	209
Pour point (°C)		ASTM D 97	−18	−12	−9	−3
Flash point (°C)		ASTM D 93	226	270	312	318
Copper corrosion		ASTM D 130	1a	1a	1a	1a
Oxidative stability (min) (RBOT)		ASTM D 2272	12	15	12	10
TGA onset temperature (°C)			305	420	450	465
Weld load (kg)		ASTM IP 239	120	140	150	160
Wear (mm)		ASTM D 4172	0.62	0.61	0.68	0.75

of the lubricants, was found to be more for ETO (180 kg) followed by TPEE (160 kg), TTMPE (150 kg), TNPGE (140 kg) and T2-EtHE (120 kg). The high weld load capacity of ETO could be attributed to the reduction in unsaturation (Adhvaryu and Erhan, 2002). All the base-stocks with high load-carrying capacity can be well exploited for metal working fluid applications.

Wear, another important characterization of lubricant base-stocks, was found higher for ETO as compared to the polyol esters. The value in case of ETO was found slightly higher compared to ERO and ESO (Adhvaryu and Erhan, 2002; Padmaja *et al.*, 2012). In the case of polyols, the value was found to be higher for TPEE (0.75 mL), followed by TTMPE, TNPGE and T2-EtHE. A similar observation was found in the case of rubber polyol esters prepared in our earlier study (Kamalakar *et al.*, 2013).

4. CONCLUSION

The study involved a mineral acid free epoxidation of thumba seed oil (ETO) and the preparation of four thumba fatty acid based base-stocks, namely, T2-EtHE, TNPGE, TTMPE and TPEE, using a minor tree-borne oil widely grown in India, Africa and other Asian countries. ETO with higher viscosities, oxidative and thermal stabilities can be well exploited for ISO VG-220 and Aviation Grade 100 applications with appropriate pour point depressants. The lubricant properties of epoxy thumba oil were found to be better compared to epoxy rapeseed and soybean oils, the most widely used lubricant base-stocks. The polyol esters with good viscosity indices, high flash points, low pour points and good thermal stabilities can be well exploited for automotive and hydraulic fluid formulations. Overall, lubricant base-stocks prepared from thumba seed oil can be exploited for numerous applications.

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