

STUDIES ON THE RHEOLOGICAL AND TRIBOLOGICAL PROPERTIES OF ACYLATED DERIVATIVES OF CASTOR OIL AND THEIR APPLICATION AS BIO-LUBRICANTS

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## Abstract

Castor oil was used as a starting material for obtaining bio-lubricants via some chemical transformations. Thus the oil was firstly epoxidized by peroxy formic acid, prepared in situ, in the presence of ambrolite as a catalyst. The epoxide obtained was subjected to base-catalyzed transesterification with methanol/NaOH followed by ring opening with alcohol (2-ethyl-1-hexanol) to give the corresponding diol. Finally, the latter diol was acylated using acetic anhydride in pyridine, whereby the acylated product was isolated.

The structures of the products of the different steps were illustrated from their spectral data (FT-IR) and (<sup>1</sup>H-NMR). The rheological and tribological properties of the compounds obtained were evaluated to confirm their suitability as bio-lubricants.

**Keywords:** *Castor oil; Bio-Lubricants; Transesterification; Spectral data; Rheological and Tribological properties.*

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## 1. Introduction

Lubricants used globally are commonly made from petroleum, coals or natural gases [1-2]. Due to their wide utilization, there is the need to search for alternative sources for producing lubricants. As a result of the long-term pollution effects associated with mineral oil-based lubricants on the environment, and the expected depletion of petroleum reservoirs all over the world in the future there is a need for cheap and renewable feedstock for the production of biodegradable lubricants [3].

There are many alternatives to petroleum based lubricant, such as synthetic or animal fat lubricants. However, lubricants derived from vegetable oils have received greater attention due to their favourable and acceptable physical properties. Among the advantages of bio-based lubricants is their high lubricity, as well as, much lower coefficient of friction compared with petrobased lubricants. Furthermore, bio-based lubricants have high flash points, which make them effective in high temperature environment to impede evaporation or dissipation [4-6].

Bio-lubricants also have relatively stable viscosity indexes, so that they are useful over a large range of temperatures. In addition, bio-based lubricants are generally derived from vegetable oils, and its processing involves a clean and pollution free method, as well as, being renewable. Finally, the non-toxic and biodegradable nature of bio-based lubricants ensures easy disposal in the environment, unlike petroleum based lubricant. These properties make bio-based lubricants an attractive alternative to petroleum based lubricants [7].

Vegetable non-edible oils have some undesired characteristics, particularly a poor resistance to high temperatures and limited use in low temperatures range because of solidification, which prevents their use, in their natural state, in many areas of lubrication. Also, Vegetable oils are prone to oxidation, i.e. have low oxidation stabilities due to the presence of allylic hydrogens in their alkyl chains. Various techniques have been applied to overcome the potential problems produced by vegetable oil, such as blending with other diluents such as (1)

polyalphaolefins, (2) chemical modification such as esterification, transesterification, (3) epoxidation.

The objective of this work is to shed light on the potential of vegetable non-edible oil in the automotive sector [8-9].

Better performances are instead obtained from esters produced by epoxidation reaction, in which a peracid is used for oxygen transfer to the double bonds in the fatty acid chains [10-11]. The peracid is usually formed in situ from hydrogen peroxide and acetic or formic acid, addressing almost all of the above-mentioned principles of green chemistry. Furthermore, fewer coloured epoxidation products are obtained which is indicative of the mild process conditions [12-14]. Fatty acids (with long chain), derived from oils, and mono-functional or poly-functional bio-based alcohols. The performance of esters depends on their chemical structure and, as a result of using alcohols and/or fatty acids which differ in their molecular weights and/or functionality (di, tri, tetra), the synthesis can be directed to obtain products with characteristics oriented to different performances (viscosity, viscosity index, pour point). For this reason, research on these products continues, and new syntheses are continually proposed both in open and patent literature [15].

In the present work epoxidation of castor oil in the presence of mixed catalyst Amberlite/HCOOH/H<sub>2</sub>O<sub>2</sub>, followed by transesterification of the product using methanol was performed. Ring opening of the products obtained by 2-ethyl-1-hexanol then finally acylation of the product using acetic anhydride afforded acylated castor oil derivatives. The structures of the prepared compounds were confirmed using Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (<sup>1</sup>H-NMR). Finally, the rheological and tribological properties of the products by modular compact rheometry (MCR) were carried out.

Evaluation of the prepared acylated castor oil derivatives as bio-lubricants was performed by measuring the viscosities and pour points of the prepared compounds.

## 2. Experimental

### 2.1 Epoxidation of castor oil

The reaction was carried out in three necked-round bottomed flask equipped with a mechanical stirrer, efficient condenser, and thermometer. Epoxide was derived by in-situ epoxidation reaction using H<sub>2</sub>O<sub>2</sub> as oxygen donor and HCOOH as an active oxygen carrier in the presence of ion exchange resin (Amberlite IR 120). The experiment was designed at the following molar ratio castor oil: formic acid (88%): H<sub>2</sub>O<sub>2</sub> (30%) was (1:0.5:1.5) and ion exchange resin Amberlite IR 120 weight percentage (15%). The reaction was maintained with vigorous stirring (1000+ rpm) at 60°C for 15 hrs. Finally, the solvent and trace water were distilled by rotary evaporator to yield the product (EC<sub>1</sub>), with designation shown in Table 1.

### 2.2. Transesterification of the product obtained

Transesterification of the epoxidized non-edible oils with methanol can be carried out using both homogeneous (acid or base). Methanol is used due to their low cost and physical and chemical advantages. The transesterification reaction occurs between alcohol adsorbed on catalyst and ester of the reactant. Homogeneous catalysts such as sodium hydroxide, potassium hydroxide, and sodium methoxide formed an alkoxide group on reaction with alcohol. The transesterification reaction was thereafter carried out by using methanol to oil molar ratio (8:1), at 60°C for 4 hrs to yield of product (EC<sub>2</sub>) with designation shown in Table 1.

### 2.3. Ring opening of the obtained products

Epoxides are highly reactive towards acids and alcohols to give diols and polyols products. So 35 gm of the product (EC<sub>2</sub>) was treated with 1.630 mL of H<sub>2</sub>SO<sub>4</sub> as catalyst and toluene as solvent and 9.604 ml of 2-ethyl-1-hexanol over 4 hrs at 110°C. The reaction was left overnight then the product was washed with brine water and dried over Na<sub>2</sub>SO<sub>4</sub> [16-17]. The excess solvent was removed with a rotary evaporator to give the product (EC<sub>3</sub>) with designation shown in Table 1.

Table 1. The designation of prepared compounds

Abbreviation	Prepared compounds	Abbreviation	Prepared compounds
EC1	Epoxidized castor oil	EC3	The diol
EC2	Transesterified EC1	EC4	Acylated pproduct

## 2.4. Acylation of the obtained products:

To a stirred solution (0.09 mol) of product (EC<sub>3</sub>), acetic anhydride (0.36 mol) was added, 4-dimethylaminopyridine (0.87 mol) and 150 mL of xylene were added. The obtained suspension was stirred and heated to 140-150°C for 8 h. Then, the product was distilled at 140-160°C to eliminate solvent then the product was extracted by ethylacetate. The product was washed with brine and dried over aqueous Na<sub>2</sub>SO<sub>4</sub> overnight, and finally, the solvent was removed by rotary evaporator to yield the target product (EC<sub>4</sub>) with designation shown in Table 1.

## 3. Characterization of the prepared compounds

The prepared compounds were characterized by using FT-IR, Model Type 'Nicolet iS10 FT-IR Spectrometer. The sample prepared as a disk. Room temperature, DTGS detector, 4 cm<sup>-1</sup> spectral resolutions. Maximum speed: 40 spectra per second at 16 cm<sup>-1</sup> resolution [18]. The prepared compounds were characterized by <sup>1</sup>H-NMR spectroscopy. Using <sup>1</sup>H-NMR type [300 M.Hs. spectrophotometer W-P-300, Bruker].

### 3.1. Evaluation of the prepared products as bio lubricant

Viscosity indices (VI) of the products were measured according to ASTM D2270-87. The kinematic viscosities of the tested compounds which were determined at 40°C and 100°C.

The pour points of the prepared compounds were measured according to the ASTM-9787. The instrument used for measuring the pour points was the Cold Filter Plugging Point Automatic Tester (CFPPA-T), model 1st CPP97-2 (France).

The flash points of the prepared compounds were determined using a Cleaveland open cup tester conforming to ASTM D92-12b.

TGA experiments were carried out using Simultaneous Q- 600 DSC/TGA (USA). The experiments use a 0.01 g polymer sample, at a heating rate of 10°C min<sup>-1</sup> from 25°C to 600°C and under a flowing (25 ml min<sup>-1</sup>) nitrogen atmosphere.

### 3.2. Measuring rheological and tribological properties by modular compact rheometry (MCR)

Different rheological and tribological tests were employed for the prepared compounds as illustrated in Figs. 8, 9. These tests were performed using a ball-on-three-plates tribometer (tribology measurement cell, Rheometer MCR502, Anton-Paar GmbH, Stuttgart, Germany [19]) Fig. 1 and 0.9 ml of each sample. Each measurement started with a conditioning run followed by the measurement of Stribeck curves at temperatures (80°C) and loads (10 N). Stribeck curves generally describe the friction coefficients of lubricated systems as a function of sliding velocity, contact pressure, or viscosity.

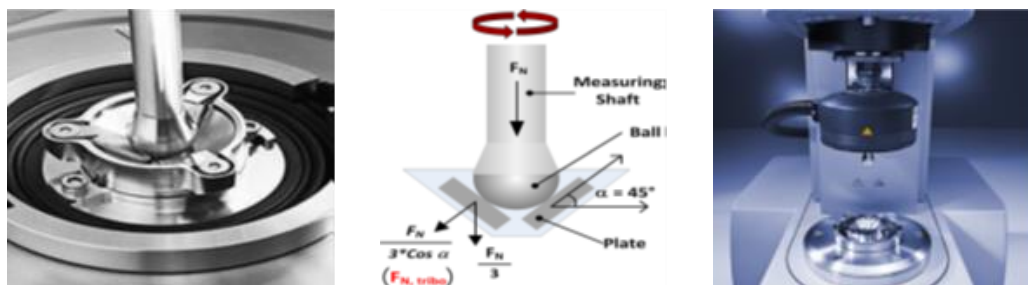
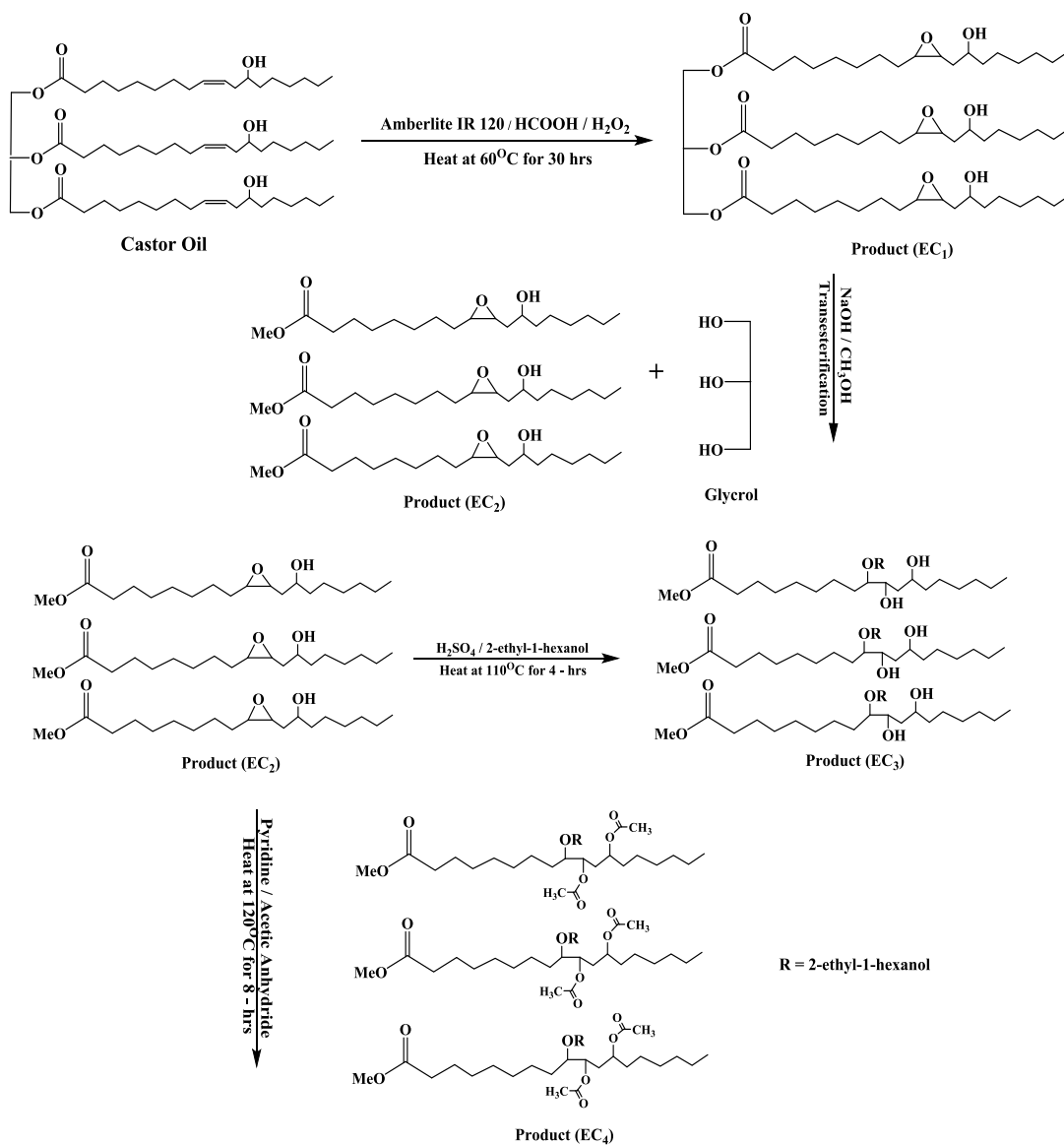


Fig. 1. Rheometer MCR502 component

#### 4. Results and discussion

In the last decades, there is an increasing concern in finding substitutes for petroleum refinery products. This is due to two reasons: first, the expected depletion of petroleum reservoirs in the future; second, petroleum products and their wastes, being non-biodegradable represent environmental petroleum due to the toxicity of most of their components. Vegetable oils, being renewable and biodegradable sources, represent suitable candidates for this purpose. Although vegetable oils suffer from the disadvantages of being susceptible to oxidation due to the presence of allylic hydrogen in their backbone, this problem could be overcome by using suitable doses of antioxidant additives.

It is hoped that this investigation will be a contribution to this trend. Thus castor oil was used as a starting material to obtain some bio-lubricants via the chemical transformations illustrated by scheme (1).



Scheme (1)

The products obtained were characterized by spectral tools (FTIR and  $^1\text{H-NMR}$ ). Evaluation of the rheological and tribological characteristics of these compounds was also performed.

#### 4.1. Spectral characterization

##### 4.1.1. The infrared spectra (FT-IR)

The infrared spectrum of castor oil is given in Fig. 2, showed the following: The hydroxyl (OH) bands appear clearly near to  $3436\text{ cm}^{-1}$  as broad bands. C-H of alkanes in the range of  $2855\text{ cm}^{-1}$  and  $2925\text{ cm}^{-1}$ . C=O appears at  $1744\text{ cm}^{-1}$ . C-O appears at  $1166\text{ cm}^{-1}$ . CH of  $\text{CH}_3$  group appears at  $1462\text{ cm}^{-1}$  and  $1362\text{ cm}^{-1}$ . CH of  $\text{CH}_2$  group appears at  $1462\text{ cm}^{-1}$  and  $1376\text{ cm}^{-1}$ . C=C of alkene appears at  $1650\text{ cm}^{-1}$ . =CH appears at  $3008\text{ cm}^{-1}$ . C=O of ester appears at  $1744\text{ cm}^{-1}$ .

The infrared spectrum of product ( $\text{EC}_1$ ) is given in Fig. 3, showed the following: The disappearance of C=C of alkene and also for =CH band, and appearance of epoxide band at  $859\text{ cm}^{-1}$ . C=O appears at  $1741\text{ cm}^{-1}$ . The hydroxyl (OH) bands appear clearly near to  $3453\text{ cm}^{-1}$  as broad bands, C-H of alkanes in the range of  $2855\text{ cm}^{-1}$  and  $2928\text{ cm}^{-1}$ . C-O appears at  $1173\text{ cm}^{-1}$ . CH of  $\text{CH}_2$  group appears at  $1462\text{ cm}^{-1}$  and  $1438\text{ cm}^{-1}$ .

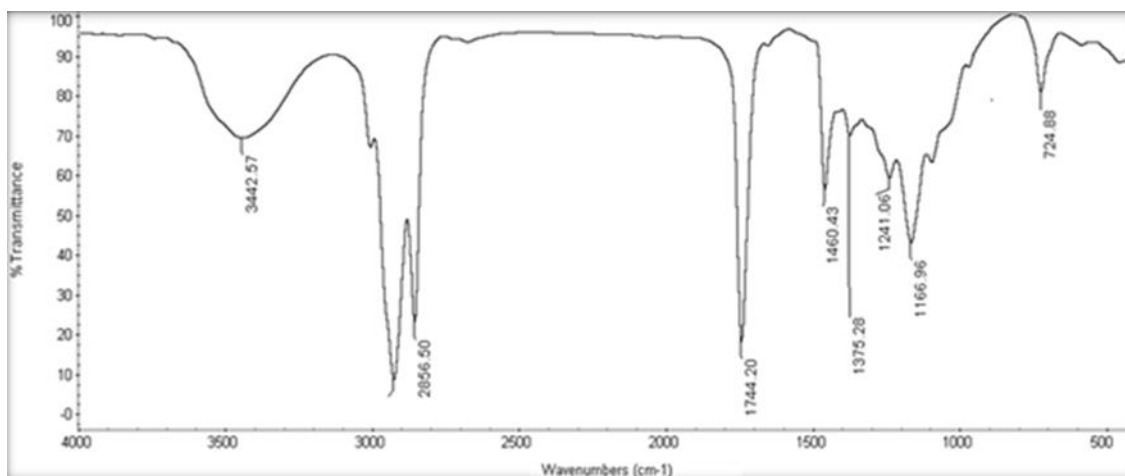


Fig. 2. The infrared spectrum of castor oil

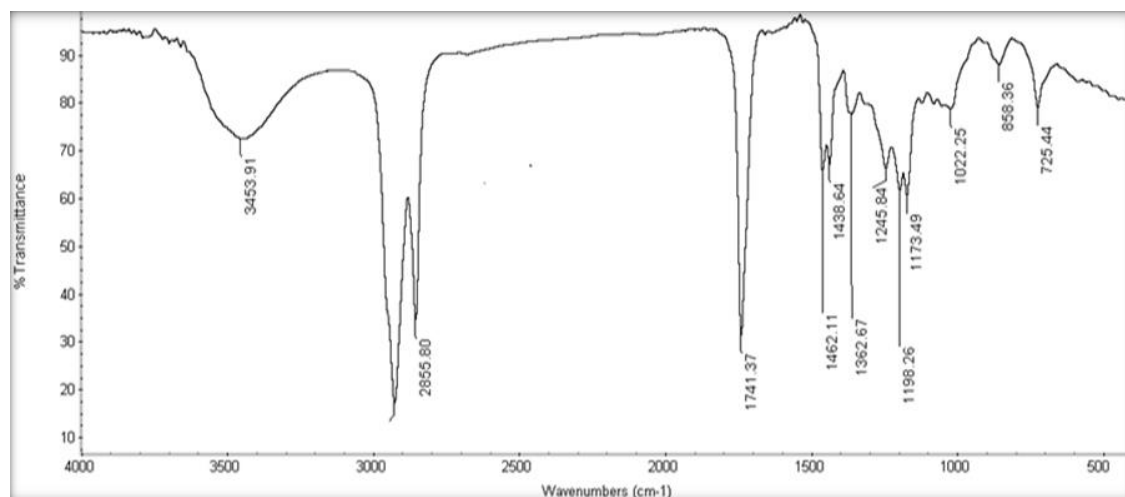


Fig. 3. The infrared spectrum of compound ( $\text{EC}_1$ )

The infrared spectrum of product ( $\text{EC}_3$ ) is given in Fig. 4, indicates the following: The disappearance of epoxide band, and appearance of hydroxyl (OH) bands appears clearly near to

3456  $\text{cm}^{-1}$ . C=O appears at 1741  $\text{cm}^{-1}$ . C-H of alkanes in the range of 2856  $\text{cm}^{-1}$  and 2928  $\text{cm}^{-1}$ . C-O appears at 1172  $\text{cm}^{-1}$ . CH of  $\text{CH}_2$  group appears at 1438  $\text{cm}^{-1}$  and 1372  $\text{cm}^{-1}$ .

The infrared spectrum of product ( $\text{EC}_4$ ) is given in Fig. 5, showed the following: There is no band for hydroxyl (OH) nearly due to acylation reaction. C=O appears with at 1740  $\text{cm}^{-1}$ . C-H of alkanes in the range of 2856  $\text{cm}^{-1}$  and 2928  $\text{cm}^{-1}$ . CH of  $\text{CH}_2$  group appears at 1462  $\text{cm}^{-1}$  and 1373  $\text{cm}^{-1}$ .

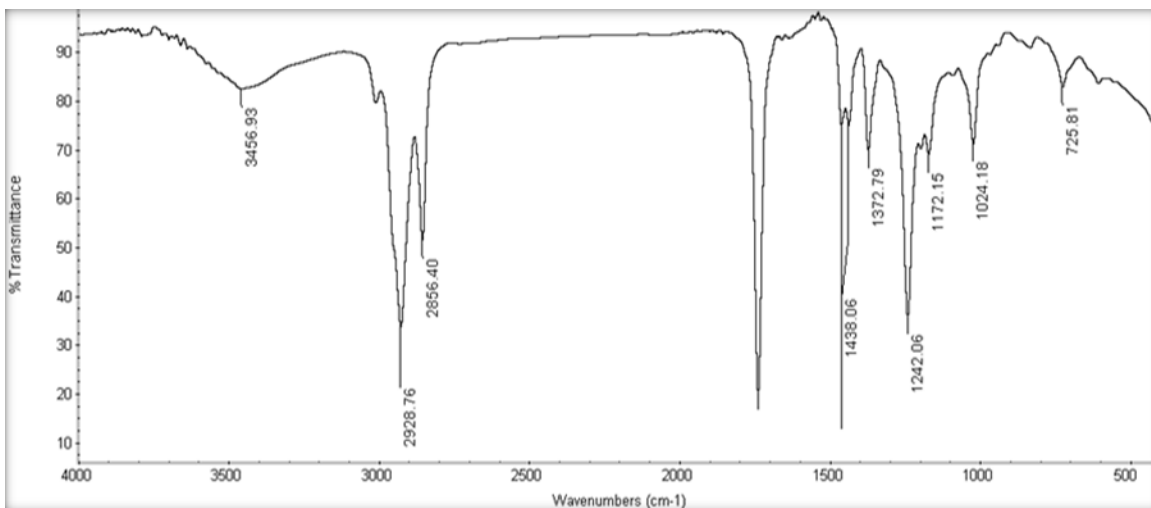


Fig. 4. The infrared spectrum of compound ( $\text{EC}_3$ )

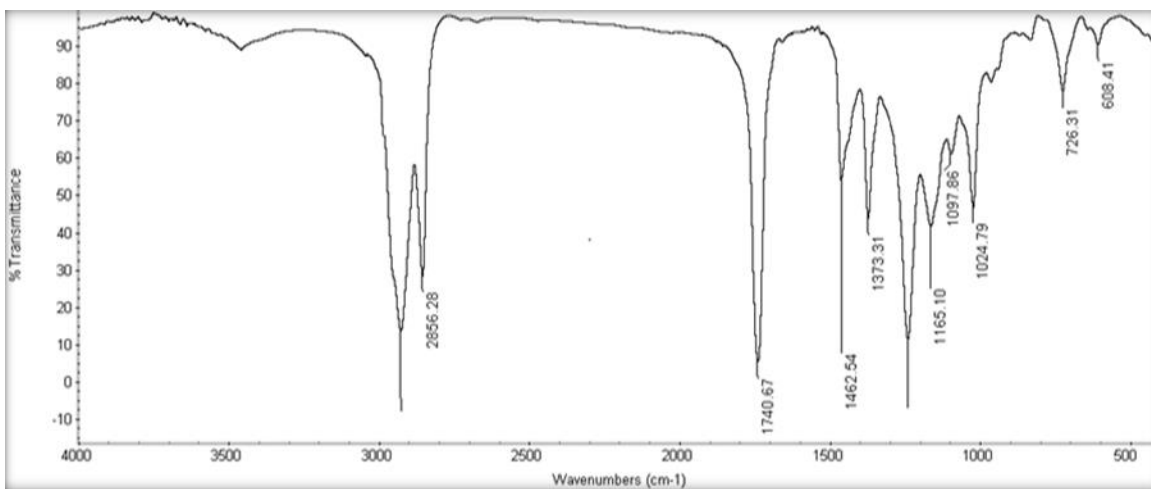


Fig. 5. The infrared spectrum of compound ( $\text{EC}_4$ )

#### 4.1.2. The nuclear magnetic resonance spectra ( $^1\text{H-NMR}$ )

The  $^1\text{H-NMR}$  spectra of products ( $\text{EC}_1 - \text{EC}_4$ ) are illustrated: The  $^1\text{H-NMR}$  spectrum of castor oil which illustrates the appearance of the  $\text{CH}_3$  terminal at  $\delta$ -0.96 ppm, -CH-OH protons at  $\delta$ -3.5 ppm, =C-H protons at  $\delta$ -5.5 ppm and methylene ( $\text{CH}_2$ ) protons at  $\delta$ -1.3 ppm.

The  $^1\text{H-NMR}$  spectrum of product ( $\text{EC}_1$ ) which illustrates the appearance of the  $\text{CH}_3$  terminal at  $\delta$ -0.96 ppm, -CH-OH protons at  $\delta$ -3.5 ppm, epoxy protons at  $\delta$ -3.2 ppm, methylene ( $\text{CH}_2$ ) protons at  $\delta$ -1.3 ppm and disappearance of =C-H protons at  $\delta$ -5.5 ppm.

The  $^1\text{H-NMR}$  spectrum of product ( $\text{EC}_4$ ) which shows the appearance of the  $\text{CH}_3$  terminal at  $\delta$ -0.96 ppm, the disappearance of -CH-OH protons at  $\delta$ -3.5 ppm and disappearance epoxy protons at  $\delta$ -3.2 ppm.



## 4.2. Evaluation of the prepared compounds

From comparison of the viscosity index value of castor oil with that synthesized compounds shown in Table 2, it is evident that the viscosity index for castor oil (221) is lower than acylated transester of treated castor oil (EC<sub>4</sub>) with value (232) which implies that the synthesized compounds show better bio-lubricant properties compared with castor oil.

Low temperature studies showed that most vegetable oils undergo poor flow and solidification at -18°C as they have a tendency to form microcrystalline structure at low temperature. The pour point should be low enough to ensure that the bio-lubricant is pump-able when the equipment is started at extremely low temperatures. So, comparing pour points of the synthesized compounds with the value of castor oil it was found that there is a clear pour point improvement for the product (EC<sub>4</sub>) with value -27°C.

Table 2. Physicochemical properties of synthesized castor oil and its acylated derivatives

Properties	Standard ASTM	Castor Oil	Prod (EC <sub>1</sub> )	Prod (EC <sub>2</sub> )	Prod (EC <sub>3</sub> )	Prod (EC <sub>4</sub> )
Viscosity index	D2270	221	175	187	193	232
Flash Point , °C	D 92	255	240	267	282	300
Pour Point , °C	D 97	-18	-9	-15	-21	-27

Flash point is useful in determination the volatility and fire resistance of a bio-lubricant and also for determination of transportation and storage temperature. So, it must be high enough to allow for safe operation at maximum operating temperature. From the results, it is evident that the product (EC<sub>4</sub>) has a value of 300°C which is necessary for most demanding applications.

The thermal stability of the prepared compounds was investigated, Figs. 6, 7, both integral is shown. It was found that the primary degradation occurs at 300°C, while the complete degradation occurs at 500°C. This confirms the suitability of the prepared compounds as bio-lubricants.

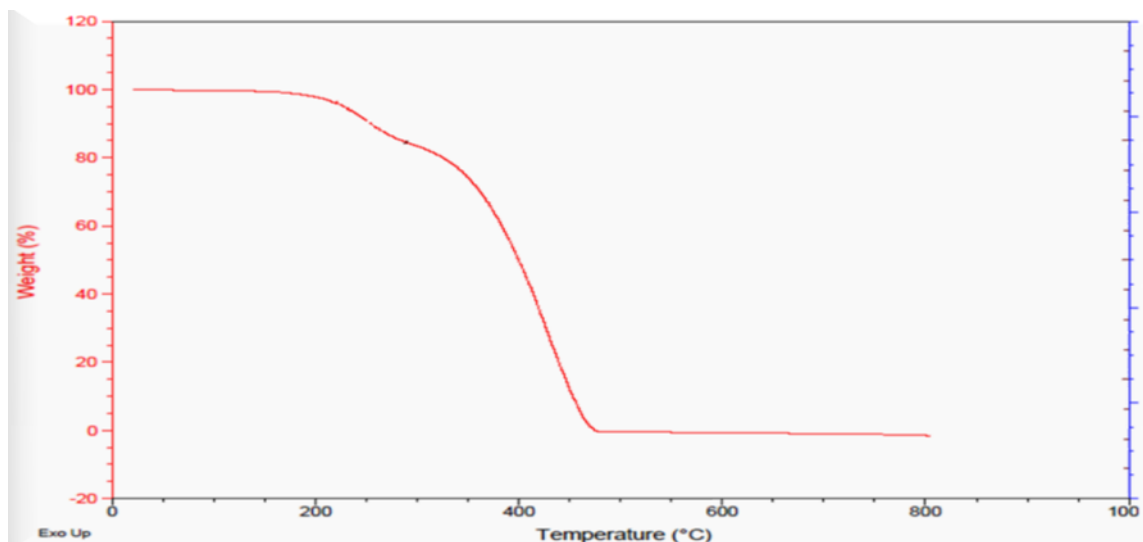


Fig. 6. TGA Curve of compound (EC<sub>3</sub>)

The most important rheological parameters for lubricants is viscosity as it also affects the tribological properties like friction between interacting surfaces and wears. In the steady-shear test, shear rates from 0 to 120 s<sup>-1</sup> at Fig. 8 were applied to the bio-lubricant. It was found that castor oil and its derivatives exhibit a Newtonian flow and by increasing shear rate, dynamic viscosity is nearly constant which is an advantage.

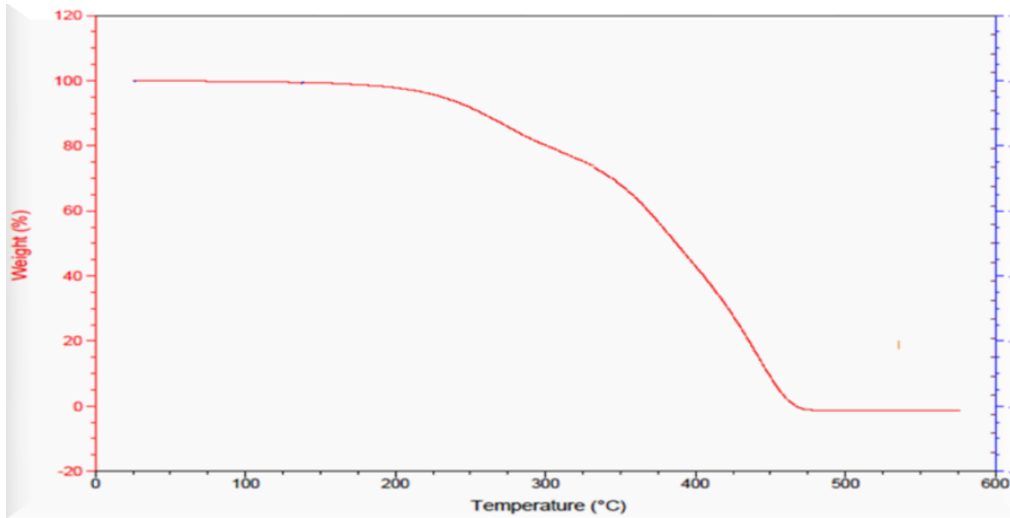


Fig. 7. TGA Curve of compound (EC4)

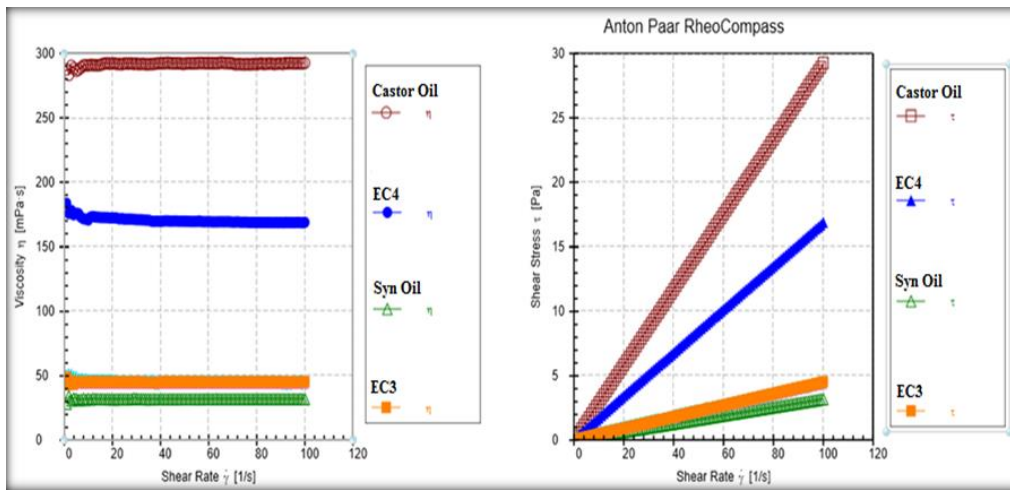


Fig. 8. Shear rate versus shear stress for castor oil, product (EC<sub>3</sub>), product (EC<sub>4</sub>) and conventional synthetic oil

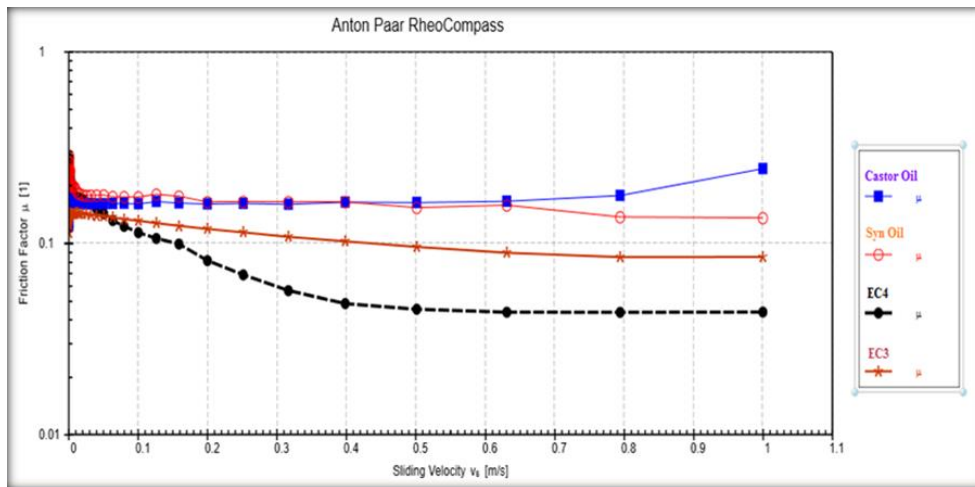


Fig. 9. Coefficient of friction (COF) versus sliding velocity for castor oil, product (EC<sub>3</sub>), product (EC<sub>4</sub>) and conventional synthetic oil



Stribeck curve shown in Fig. 9 has three types of lubricant conditions which are a boundary, mixed and hydrodynamic lubricant [20]. In the middle between mixed and hydrodynamic lubricant condition, there was an elastohydrodynamic lubricant which is the friction coefficient decreasing during the increasing of the parameter. Acylated castor oil showed low friction coefficient at 80°C compared with castor oil and conventional synthetic oils.

## 5. Conclusion

Castor oil can be used, after some chemical transformations, as a suitable candidate for obtaining environmental friendly bio-lubricants. Saturation of double bonds of castor oil gives products less susceptible to oxidation than the oil itself, i.e. having more oxidation stabilities.

Chemically modified castor oil products were given excellent results as rheological and tribological properties. Being a non-edible oil, castor oil can be used as a source for obtaining bio-lubricants without causing any nutritional problems

## References

- [1] Quinchia LA, Delgado MA, Reddyhoff T, Gallegos C, Spikes HA. Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers. *Tribology International*. 2014; 69:110–117.
- [2] Tewari DD. A historical policy review of success of castor revolution in Gujarat. India. *Journal of Human Ecology*. 2012; 38(3):213-222.
- [3] Severino LS, Auld DL, Baldanzi M, Cândido MJD, Chen G, Crosby W, Tan D, He X, Lakshamma P, Lavanya C, Machado OLT, Mielke T, Milani M, Miller TD, Morris JB, Morse SA, Navan AA, Soares DJ, Sofiatti V, Wang ML, Zanotto MD, and Zieler H.A review on the challenges for increased production of castor. *Agronomy Journal*. 2012; 104(4):853-880.
- [4] Panwar NL, Shrirame HY, Rathore NS, Jindal S, Kurchania AK. Performance evaluation of a diesel engine fueled with methyl ester of castor seed oil. *Journal of Applied Thermal Engineering*. 2010; 30(2-3):245–249.
- [5] Sonalee D, Priyanka P, Smita M, Sanjay KN. Influence of NCO/OH and transesterified castor oil on the structure and properties of polyurethane: Synthesis and characterization. *Journal of Material Express*. 2015; 5(5):377-389.
- [6] Amit S, Sarviya RM, Rehman A, Khaira HK. Experimental study of castor oil based lubricant for automotive applications. *Journal of Engineering Research and Applications*. 2014; 4(1):104-107.
- [7] Aidan MD, Talib MA, Ammar SA, Ziad TA. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. *Journal of Renewable Energy*. 2016; 97:19–23.
- [8] Ebtisam KH, Mamdouh SE, Salah A K, Naser ME. Manufacturing of environment friendly bio-lubricants from vegetable oils. *Egyptian Journal of Petroleum*. 2017; 26:53–59.
- [9] El-Magly IA, Nagib HK, Mokhtar WM. Aspects of the behavior of some pentaerythritol ester base synlubes for turbo-engines. *Egyptian Journal of Petroleum*. 2013; 22:169-177.
- [10] Venu BB, Vaibhav VG. Improved thermos-oxidative stability of structurally modified waste cooking oil methyl esters for bio-lubricant application. *Journal of Cleaner Production*. 2016; 112:4515–4524.
- [11] Talib N, Nasir RM, Rahim EA. Tribological behaviour of modified jatropha oil by mixing hexagonal boron nitride nanoparticles as a bio-based lubricant for machining processes. *Journal of Cleaner Production*. 2017; 147:360-378.
- [12] Isbell TA, Lowery BA, DeKeyser SS, Winchell ML, Cermak SC. Physical properties of triglyceride estolides from lesquerella and castor oils. *Journal of Industrial Crops and Products*. 2006; 23:256-263.
- [13] Geethanjali G, Sony MK, Padmaja KP, Karuna MSK, Prasad RBP. Novel acyl derivatives from karanja oil: alternative renewable lubricant base stocks. *Journal of Industrial & Engineering Chemistry Research*. 2014; 53:8685-8693.
- [14] Garcia-Zapateiro LA, Franco JM, Valencia C, Delgado MC, Gallegos C. Viscous thermal and tribological characterization of oleic and ricinoleic acids-derived and their blends with vegetable oils. *Journal of Industrial and Engineering Chemistry*. 2013; 19:1289-1298.
- [15] Satya BP, Venkata PK, Venkata SKRB, Saravanan K, Badari NPR. Castor oil fatty acid based estolide esters and their derivatives as potential lubricant base stocks. US Patent. Council of Scientific and Industrial Research (CSIR). 2014; 8742150 B2.

- [16] Nassar AM, Ahmed NS, Kamal RS. Study the Efficiency of Some Esters as Synthetic Lubricating Oil. *Journal of Pet Coal*. 2018; 60(3):520-541.
- [17] Kamal RS, Ahmed NS, Nassar AM. Synthesis and Characterization of Mixed Esters as Synthetic Lubricants. *Journal of Pet Coal*. 2018; 59(6):736-746.
- [18] Nassar AM, Ahmed NS, Abdel-Hameed HS, El-Kafrawy AF. Synthesis and utilization of non metallic detergent / dispersant and antioxidant additives for lubricating engine oil. *Journal of Tribology International*. 2016; 93(Part A):297-305.
- [19] Tobias Z, Jhina HM, Raimund J, Somphong P. Wear mechanisms and abrasion rates in selective laser sintering materials. *Journal of Polymer Testing*. 2018; 67:545–550.
- [20] Eder SJ, Bianchi D, Neacsu IA, Vorlaufer G. An experimental and signal analysis workflow for detecting cold-induced noise emissions (cold squealing) from porous journal bearings. *Journal of Mechanical Systems and Signal Processing*. 2019; 115:60–69.

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