Study on the Lubricating Properties of Castor (Ricinus communis) and Hydroxylated Rubber (Hevea brasiliensis) Seed Oil

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ABSTRACT: Rubber seed oil (RSO) (Hevea brasiliensis) was extracted from rubber seeds by chemical means. The effect of temperature on the oil yield was investigated. The experiment suggested that the maximum yield of the oil occurs at 60 °C. This is a result of the proximity to the boiling point of n-hexane, which is about 68 °C. Epoxidized and hydroxylated RSOs were further synthesized by performic acid generated in situ by the reaction of formic acid with 30% hydrogen peroxide. The physiochemical properties of the epoxidized rubber seed oil (ERSO) and hydroxylated rubber seed oil (HRSO) were determined. A separate study was also carried out on castor seed oil (CSO). The improved products were characterized with respect to their configuration and properties. Spectroscopic analysis was carried out on the oil base stocks (RSO, CSO, ERSO, and HRSO). All of the experimental findings were compared with one another. The lubricating properties of CSO and HRSO are further studied as a result of their biodegradability, leading to an increasing interest in biodegradable lubricant products. However, the creation of a biodegradable base liquid that could surpass or substitute most of the ordinary mineral oils has been troublesome. To create such lubricant products, the scientific community has tuned its attention to the use of vegetable oils (natural or chemically modified). Vegetable oils have several advantages that make them favorable as a potential source of eco-friendly lubricant products. Their combination of renewability, biodegradability, antitrust properties, good viscosity indices, high flash points, and excellent lubrication performance that are way better than those of petroleum-based lubricants makes them decent candidates as mineral-oil-based products.

However, a few prominent disadvantages limit their potential in the lubricant industry. These disadvantages include low thermal oxidation stability, weak performance at low temperatures, unimpressive cold flow behavior, susceptibility to hydrolysis, and oxidative attack. To improve on these shortcomings that have limited the application of vegetable oils as lubricants, chemical modification via hydroxylation and epoxidation has been utilized in this research.

In Nigeria, vegetable oil subordinate generally depends on exceptionally costly imported oils such as soybean and linseed oil. Rubber seed oil (Figure 2) apart from being considered as a

1.. INTRODUCTION

As of late, the world has been affected by purposeful and inadvertent oil or lubricants losses to the environment because of spillage and dissipation of said lubricants. Lubricants are generally used to reduce the friction coefficient between bodies in contact. Their importance in the world of working machinery cannot be underestimated. The base oil is of utmost importance in the production of lubricants, as it makes up 75–90% of the lubricant. The most common source of these base oils is mineral oil, which is nonrenewable and non-biodegradable. Owing to this, other sources of base oils such as synthetic oils and vegetable oils have been discovered as alternatives to mineral oil. Fifty percent of all lubricants currently sold are mineral-oil-based. Mineral-oil-based products are generally considered unfavorable because of their adverse effect on the environment and they cause serious hazards to the ecosystem at large because of their high ecotoxicity and low biodegradability, leading to an increasing interest in biodegradable and eco-friendly lubricant products. However, the creation of a biodegradable base liquid that could surpass or substitute most of the ordinary mineral oils has been troublesome. To create such lubricant products, the scientific community has tuned its attention to the use of vegetable oils (natural or chemically modified). Vegetable oils have several advantages that make them favorable as a potential source of eco-friendly lubricant products. Their combination of renewability, biodegradability, antitrust properties, good viscosity indices, high flash points, and excellent lubrication performance that are way better than those of petroleum-based lubricants makes them decent candidates as mineral-oil-based products.

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biodegradable lubricant has been used as alkyd resin, liquid soap, an aid for the processing of polymers, biodiesel, and surface-coating binder. Statistically speaking, the rate at which castor seed oil (CSO) is produced currently cannot meet the great demand of the product and the hydroxyl nature of castor oil (Figure 1) makes it a natural polyol with considerable oxidative stability. This uniqueness allows castor oil to be used in industrial applications such as coatings, paints, biodiesel lubricants, and inks.

As a result of the close similarities between these two common seeds, their respective oils, CSO and hydroxylated RSO (HRSO), are closely compared with each other. Nigeria imports over $85 million worth of castor oil each year. However, there has been a gradual increase in the number of castor seed and rubber seed cultivations in Nigeria. For this study, Obanla et al. report the epoxidation of rubber seed oil (ERSO). HRSO is derived from ERSO but with an alteration of the final temperature. The spectroscopic data and physicochemical properties of the products, CSO, RSO, ERSO, and HRSO, were determined. The data obtained for HRSO was compared to that of crude castor oil (CSO). This research paper centers on synthesizing hydroxylated rubber seed oil (HRSO), studying physicochemical and spectroscopic properties, and comparing the lubricating performance of CSO and HRSO.

2. MATERIALS AND METHOD

2.1. Materials. Crude RSO used in this research was extracted from Rubber Plantation at the Rubber Research Institute of Nigeria, Edo State, Nigeria. Castor oil used was purchased from an oil mill industry in Ojota, Lagos state, Nigeria. Formic acid (AR grade: 99.9% purity) was obtained from Merck. Hydrogen peroxide (30% w/v) and hydrobromic acid were obtained from Sigma-Aldrich Chemicals purchased by Covenant University, Ogun state, Nigeria.

2.2. Synthesis of Hydroxylated Rubber Seed Oil (HRSO). The hydroxylation reaction follows the same procedure as epoxidation described by Obanla et al. but with a slight adjustment, in the sense that at the end of the 3 h reflux during the epoxidation reaction, the temperature is increased to 80 °C and was maintained for another 14 h, as shown in Figure 3. The resulting HRSO was then characterized using American Oil Chemist Society (AOCS) methods.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature on Extraction Yield. Apparently, the temperature had a substantial effect on the oil yield. In Figure 4, the mean oil yield at 40 °C was about 33.3% and 38.8% at 50 °C, 44.4% at 60 °C, 43.8% at 70 °C, and 41.5% at 80 °C, all percentages are by weight. The oil yield of rubber seed was maximum at 60 °C as displayed in Figure 4. When the extraction temperature was increased to 80 °C, it caused a decrease in yield to 41.50%. This simply implies that an increase in temperature above 60 °C does not favor the reaction conditions. Therefore, the optimum extraction temperature of rubber seed oil for maximum oil yield occurs at 60 °C.

3.2. Physicochemical Properties of Crude Rubber Seed Oil (RSO). The fatty acid profile and physicochemical properties like acid value, specific gravity, saponification value, iodine value, and percentage oxirane of RSO and ERSO were determined by
the AOCs methods and reported by Obanla et al. In that study, it was stated that the specific gravity of 0.874 indicates that the oil is less dense than water, which also suggests the absence of heavy elements in the oil. The pH value of 5.26 indicates that the oil is slightly acidic, which implies the presence of an equitable amount of free fatty acid. The saponification value obtained was 202 mgKOH/g, which was very high, indicating the existence of a high percentage of free fatty acids. The RSO obtained was 202 mgKOH/g, which was very high, indicating the existence of a high percentage of free fatty acids. The RSO extracted is on the verge of rancidity or hydrolysis of oil when exposed to light, air, or moisture.

From Table 1, the iodine value of CSO was 83.5 gI2/100 g; it can therefore be inferred that castor oil is a highly viscous oil and occurs only in the liquid state, which implies that CSO can be categorized as a nondrying oil. The castor oil used in this research registered a specific gravity of 0.91 mgKOH/g. The low acid value is very favorable and shows that the oil has little susceptibility to decomposition thus giving it very long shelf life.

The physicochemical properties of HRSO are shown in Table 2 and were compared with those of ERSSO, which was obtained in previous research investigated by Obanla et al. The specific gravities of ERSSO and HRSO were greater than that of RSO. This increase in specific gravity is a result of the upsurge in density, which is attributed to the presence of oxygen in ERSSO and HRSO. A significant decrease in the acid value of ERSSO and HRSO was noticed.

The initial acid value of RSO of 202 mgKOH/g as reported by Obanla et al. was reduced to 45.33 for ERSSO and 37.80 for HRSO, as displayed in Table 2. This notable decrease in the acid value is a result of the reduction of fatty acids or carboxylic acid groups present in the RSO. Taking the saponification values of the modified rubber seed oils into consideration, it is observed that the saponification value of HRSO is greater than that of ERSSO and slightly greater than that of RSO. This is most likely the result of the hydroxyl group present in HRSO. This increases the average molecular weight (or chain length) of the HRSSO structure. The hydroxyl group in HRSO is also prone to alkali hydrolysis. This result is similar to those reported in the previous studies. The speci

| Table 1. Physiochemical Properties of Crude Castor Seed Oil (CSO) |
|------------------|------------------|
| property         | value            |
| density kg/m³ at 26 °C | 959              |
| specific gravity at 30 °C | 0.95             |
| pH value         | 5.296            |
| flash point °C   | 190              |
| viscosity at 40 °C (mm²/s) | 281.8          |
| viscosity at 100 °C (mm²/s) | 72.53          |
| viscosity index  | 321              |
| color            | pale yellow      |
| odor             | odorless         |
| acid value (mgKOH/g) | 0.91            |
| saponification value (mgKOH/g) | 179.52        |
| iodine value (gI2/100 g) | 83.5           |
| refractive index at 40 °C | 1.472          |

| Table 2. Comparison of Physiochemical Properties of Epoxidized and Hydroxylated Rubber Seed Oil |
|-----------------------------------------------|--------------|
| property                                      | ERSO         | HRSO         |
| color                                         | golden yellow| yellow       |
| specific gravity at 30 °C                     | 0.95         | 0.945        |
| acid value (mgKOH/g)                          | 0.91         | 37.80        |
| flash point (°C)                              | 197          | 152.0        |
| fire point (°C)                               | 210          | 171.0        |
| saponification value (mgKOH/g)                | 179.52       | 255.25       |
| iodine value (gI2/100 g)                      | 83.5         | 23.81        |
| kinematic viscosity                           | 321.0        | 380.65       |
| pour point (°C)                               | 151.0        | 106.0        |

| Table 3. Comparison of Lubricating Properties of CSO and HRSO |
|------------------|------------------|
| property         | CSO             | HRSO         |
| color            | pale yellow     | yellow       |
| specific gravity at 30 °C | 0.95           | 0.945        |
| acid value (mgKOH/g) | 0.91          | 37.80        |
| viscosity at 40 °C (mm²/s) | 281.8       | 72.53        |
| viscosity index  | 321            | 152.0        |
| kinematic viscosity | 321.0       | 380.65       |
| pour point (°C) | 151.0          | 106.0        |
attribute to consider when selecting a biodegradable base lubricant.  

3.4. Comparing the Spectra of RSO, ERSO, and HRSO.  
RSO, ERSO, and HRSO were characterized using Fourier transform infrared (FTIR) analysis as shown in Figures 5−8, respectively. The spectra obtained for the modified oil are nearly similar to that of the raw RSO, except for the absorption due to the oxygen and hydroxyl group formation in ERSO and HRSO, respectively, as shown in Figures 6 and 7. In Figure 6, the band at 824.76 cm$^{-1}$ is the result of the presence of epoxide in the modified rubber seed oil chain. This same band is not present in Figure 7. This is because the epoxy ring opens to form the hydroxyl group for HRSO. This observation is confirmed with the presence of strong broadband at about 3475 cm$^{-1}$ in Figure 7. This band indicates the presence of an O−H functional group in HRSO (Table 4).

3.5. FTIR Analysis of Castor Oil. FTIR spectrum of CSO is presented in Figure 8. The strong broadband at about 3384 cm$^{-1}$ is ascribed to the presence of a hydroxyl group in the castor oil (O−H stretching). This confirms the hydroxyl nature of castor oil (Figure 8). The other labeled bands in the spectrum are displayed in Table 5.

4. CONCLUSIONS  
Rubber seed oil was used to synthesize ERSO and HRSO by epoxidation and hydroxylation. FTIR analysis was used to carry out structural characterizations. The contents of this research confirm that rubber seed oil can conveniently produce an epoxide group with a superior percentage of oxirane. This component indicates the quality of ERSO with regard to its application as a lubricant or for other industrial purposes. The physiochemical findings also affirmed that HRSO could be synthesized by opening up the epoxy rings at optimal epoxide yield at a minimal temperature of ≥80 °C to yield glycol, which results in the O−H functional group. Castor oil was characterized using FTIR analysis, and the findings confirmed the hydroxyl nature of castor oil. The presence of the hydroxyl group makes castor oil more oxidatively stable than other counterparts and puts it in an advantageous position for use as a base lubricant.
The physicochemical properties of raw castor oil were compared with those of hydroxylated rubber seed oil (HRSO). It was concluded that HRSO would serve as a better lubricant base. This is the result of the very low iodine value of the synthesized HRSO, meaning there are fewer unsaturated bonds present in HRSO. Also, the higher viscosity index of

| frequency range | assignment | comments                      |
|-----------------|------------|-------------------------------|
| 2850–2860       | C–H        | stretching of alkane          |
| 3010            | C–H        | stretching of nonconjugated unsaturation |
| 1745–1750       | C=O        | stretching of esters          |
| 1460–1465       | C–H        | bending of unsaturated alkane |
| 1115–1170       | C=O        | stretching of esters          |
| 720–725         | C–C        | bending of saturated C atoms  |

| frequency range | assignment | comments                      |
|-----------------|------------|-------------------------------|
| 3008            | C–H        | stretching frequency of nonconjugated unsaturation |
| 2923            | C–H        | stretching frequency of alkane |
| 1742            | C=O        | stretching frequency of ester |
| 1655            | C=C        | stretching frequency of alkene |
| 1458            | C–H        | bending frequency of unsaturated alkene |
| 1416            | O–H        | bending frequency of carboxylic acid |
| 1162            | C–O        | stretching frequency of ester |
| 724             | C–C        | bending frequency of unsaturated alkene |

The physicochemical properties of raw castor oil were compared with those of hydroxylated rubber seed oil (HRSO). It was concluded that HRSO would serve as a better lubricant base. This is the result of the very low iodine value of
HRSO compared to that of castor oil puts it in an advantageous position with regard to lubrication applications.

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O.R.O. prepared the manuscript. F.U.M. sourced all of the raw materials. O.S.A., M.E.O., T.E.O., and B.D.E. did the editing and reviewing of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Fadhil, A. B.; Adnan, A. I. Production and evaluation of biodiesel from mixed castor oil and waste chicken oil. *Energy Sources, Part A* 2016, 38, 2140–2147.

(2) Abdullah, B. M.; Salimon, O. Physicochemical characteristics of Malaysian rubber (Hevea brasiliensis) seed oil. *Eur. J. Sci. Res.* 2009, 31, 431–445.

(3) Aigbodion, A. I.; Okieimen, F.; Obazee, E.; Bakare, I. O. Utilisation of maleinized rubber seed oil and its alkyl resin as binders in water-borne coatings. *Prog. Org. Coat.* 2003, 46, 28–31.

(4) Aigbodion, A. I.; Pillai, C. K.; Bakare, I. O.; Yahaya, L. Synthesis characterization and evaluation of heated rubber seed oil and rubber seed oil modified alkyl resins as binders in surface coatings. *Indian J. Chem. Technol.* 2001, 8, 378–384.

(5) Asuquo, J. E.; Anusiem, A. C.; Etim, E. E. Extraction and characterization of rubber seed oil. *Int. J. Mod. Chem.* 2012, 1, 109–115.

(6) Akchurin, A.; Bosman, R.; Lught, P. M.; van Drogen, M. On a Model for the Prediction of the Friction Coefficient in Mixed Lubrication Based on a Load-Sharing Concept with Measured Surface Roughness. *Tribol. Lett.* 2015, 59, No. 19.

(7) Bosman, R.; Schipper, D. J. Microscopic Mild Wear in the Boundary Lubrication regime. *Laboratory for Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente.*

(8) Aluyor, E.; Ori-Jesu, M. Biodegradation of Mineral Oils - A Review. *Afr. J. Biotechnol.* 2009, 8, 915–920.

(9) Evans, R. D.; More, K. L.; Darragh, C. V.; Nixon, H. P. Transmission Electron Microscopy of Boundary-Lubricated Bearing Surfaces. Part 2: Mineral Oil Lubricant with Sulphide and Phosphorus Containing Gear Oil Additives. *Transil. Trans.* 2005, 48, 299–307.

(10) Gunstone, F. D. Vegetable Oils in Food Technology: Composition, Properties and Uses; 1st ed.; CRC Press, 2002; pp 1–10.

(11) Ali, H.; Khan, E.; Ilahi, I. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity and Bioaccumulation. *Hindawi. J. Chem.* 2019, 1–14.

(12) Liew, H. K.; Yusop, R. M.; Salih, N.; Saimon, J. Optimization of the in-situ Epoxydation of Linoleic Acid of jathropha Curcas Oil with perfomic acid. *Malays. J. Anal. Sci.* 2015, 19, 144–154.

(13) Luther, R. Bio-Based and Biodegradable Base Oils. In *Encyclopedia of Lubricants and Lubrication*; Mang, T., Ed.; Springer, Berlin, Heidelberg, 2014; pp 131–146.

(14) Schneider, M. P. Plant Oil based lubricants and hydraulic fluids. *J. Sci. Food Agric.* 2006, 86, 1769–1780.

(15) Mohammed, N. Synthesis of Bio-Lubricant from Vegetable Oil; Ahmadu Bello University, Zaria, 2015.

(16) Mutlu, H.; Meier, M. A. R. Castor oil as a renewable resource for the chemical industry. *Eur. J. Lipid Sci. Technol.* 2010, 112, 10–30.

(17) Obanla, O. R.; Udonne, J. D.; Ajani, O. O.; Omodor, O. J.; Omolewa, D. A. Extraction, comparative study and Property evaluation of synthesized bar soap from locally sourced rubber (Hevea brasiliensis) seed oil and palm kernel oil. *Int. J. Mech. Eng. Technol.* 2018, 9, 308–319.

(18) Obanla, O. R.; Udonne, J. D.; Ajani, O. O.; Ojeewumi, M. E.; Omodor, O. J. Oxirane Ring Opening of Rubber (Hevea brasiliensis) Seed Oil by Perfomic Acid. *Int. J. Innovative Technol. Explor. Eng.* 2019, 9, 5070–5073.

(19) Okieimen, F. E.; Pavithran, I. C.; Bakare, I. O. Epoxydation and hydroxylation of rubber seed oil: one-pot multi-step reactions. *Eur. J. Lipid Sci. Technol.* 2005, 107, 330–336.

(20) Nowak, P.; Kucharska, K.; Kamiński, M. Ecological and Health Effects of Lubricant Oils Emitted into the Environment. *Int. J. Environ. Res. Public Health* 2019, 16, No. 3002.

(21) Yahaya, M. S.; Roaf, N. A.; Ibrahim, Z.; Ahmad, A.; Gomes, C. Modifications Required for Palm Oil to be Qualified as a Mechanical Lubricant. *Int. J. Manuf. Mater., Mech. Eng.* 2018, 9, 50–66.

(22) Soni, S.; Agarwal, M. Lubricants from renewable energy sources – a review. *Green Chem. Lett. Rev.* 2014, 7, 359–382.

(23) Syahir, A. Z.; Zulkifli, N. W. M.; Masjuki, H. H.; Kalam, M. A.; Alabdulkareem, A.; Gulzar, M.; Khuong, L. S.; Harith, M. H. A review on bio-based lubricants and their applications. *J. Cleaner Prod.* 2017, 168, 997–1016.

(24) Trevino, A. S.; Trumbo, D. L. Acetoacetylated castor oil in coatings applications. *Prog. Org. Coat.* 2002, 44, 49–54.

(25) Usu, F. O.; Ihenyen, G. A.; Chukwuma, F. H.; Imoee, O. S. Processing, Analysis and Utilization of Rubber Seed Oil and Cake. Paper presented at the National Conference on Industrial Utilization of NATural Rubber Seed, Latex, and Wood, Rubber Research Institute of Nigeria, Benin City, 1985; pp 13–21.

(26) Vinay, R. P.; Geral, G. D.; Lakshmi, C. K. V.; Randall, M.; Bryan, J. J. S. Castor Oil: Properties, Uses, and Optimization of Processing Parameters in Commercial Production. *Lipid Insights* 2016, 9, No. LPLS40233.

(27) Yusuf, A. K.; Mamma, A. S.; Ahmed, A. S.; Agunwa, U. Extraction and characterization of castor seed oil from wild Ricinus communis. *Int. J. Sci. Environ. Technol.* 2015, 4, 1392–1404.

(28) Yusup, S.; Modhar, K. Basic properties of crude rubber seed oil and crude palm oil blend as a potential feedstock for biodiesel production with enhanced cold flow characteristics. *Biomass Bioenergy* 2010, 34, 1523–1526.