

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

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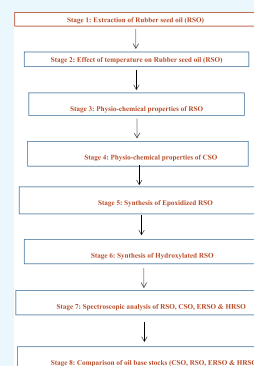
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ABSTRACT: Rubber seed oil (RSO) (*Hevea brasiliensis*) was extracted from rubber seeds by chemical means. The effect of temperature on the oil yield was investigated. The experiment suggested that the maximum yield of the oil occurs at 60 °C. This 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 common hydroxyl nature to ascertain their suitability as a lubricant base. Both oils can be categorized as a nondrying oil with saponification values of 179.52 and 255.25 mgKOH/g, respectively, and as such possess advantageous properties for industrial application. When compared to one another, HRSO appears to be a more effective choice as a lubricant base. This is because of its higher viscosity index of 380.65. The outcomes of this study indicate that hydroxylated and epoxidized RSO with high oxirane content can be synthesized concurrently by one-pot multistep reactions.



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.^{5–7} The most common source of these base oils is mineral oil, which is nonrenewable and non-biodegradable.^{1,9,13} Owing to this, other sources of base oils such as synthetic oils and vegetable oils have been discovered as alternatives to mineral oil.^{8,10,13} Fifty percent of all lubricants currently sold are eventually released into the environment, 95% of these lubricants are mineral-oil-based.^{14,15} 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.^{11,20} 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.¹⁹ Their combination of renewability, biodegradability, anticorrosion properties, good viscosity indices, high flash points, and excellent lubrication performance^{21–23} that are way better than those of petroleum-based lubricants makes them decent candidates as mineral-oil-based products.²⁸

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.^{9,13} 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

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biodegradable lubricant^{2,18,28} has been used as alkyd resin,³ liquid soap,¹⁶ an aid for the processing of polymers,^{17,24} biodiesel,^{27,28} and surface-coating binder.^{3,4}

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.^{15,23,25} This uniqueness allows castor oil to be used in industrial applications such as coatings, paints, biodiesel lubricants, and inks.^{1,9,23,25,26}



Figure 1. Castor seeds.



Figure 2. Rubber seeds.

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.²⁶ 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.



Figure 3. Epoxidation (3 h at 60 °C)/hydroxylation reaction (3 h at 60 °C then 14 h at 80 °C).

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

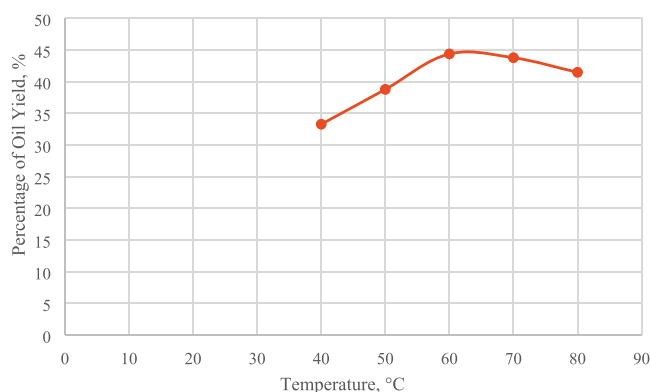


Figure 4. Effect of temperature on percentage oil yield.

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 appears to be significantly greater than the values obtained by Asuquo et al. This shows that the crude RSO is not viable in soap production when compared to other oils such as palm oil, which has a saponification value of 111 mgKOH/g. The acid value 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 rancidification (complete oxidation 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

Table 1. Physicochemical Properties of Crude Castor Seed Oil (CSO)

property	value
density kg/m ³ at 26 °C	959
specific gravity at 30 °C	0.95
pH value	5.296
flash point °C	190
viscosity at 40 °C (mm ² /s)	281.8
viscosity at 100 °C (mm ² /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 (gI ₂ /100 g)	83.5
refractive index at 40 °C	1.472

occurs only in the liquid state, which implies that CSO can be categorized as a nondrying oil.^{1,15,23,25,26} The castor oil used in this research registered a specific gravity of 0.95. Yusuf et al. reported similar results. Castor oil had a high viscosity of 281.8 mm²/s at 40 °C, which is the result of the hydrogen bonding present in its hydroxyl groups. The acid value of castor oil was 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 ERSO, which was obtained in previous research investigated by Obanla et al. The specific

Table 2. Comparison of Physicochemical Properties of Epoxidized and Hydroxylated Rubber Seed Oil

property	ERSO	HRSO
color	golden yellow	yellow
specific gravity at 30 °C	0.927	0.945
acid value (mgKOH/g)	45.33	37.80
saponification value (mgKOH/g)	207.60	255.25
iodine value (gI ₂ /100g)	30.48	23.81
oxirane content	5.37	3.76
viscosity at 40 °C (mm ² /s)	47.33	48.73
viscosity at 100 °C (mm ² /s)	17.46	17.81
viscosity index	383.76	380.65

gravities of ERSO 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 ERSO and HRSO. A significant decrease in the acid value of ERSO 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 ERSO 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 ERSO 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 HRSO structure. The hydroxyl group in HRSO is also prone to alkali hydrolysis. This result is similar to those reported in the previous studies.^{12,18}

3.3. Comparison of Lubricating Properties of CSO and HRSO.

A close observation of data presented in Table 3 shows

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
flash point (°C)	197	152.0
fire point (°C)	210	171.0
saponification value (mgKOH/g)	179.52	255.25
iodine value (gI ₂ /100 g)	83.5	23.81
kinematic viscosity	321.0	380.65
pour point (°C)	151.0	106.0

that CSO and HRSO exhibit very similar color. CSO appears to be more viscous than HRSO as a result of its greater Iodine value. This high viscosity of CSO makes it a problematic base lubricant. This simply means HRSO is more suitable for lubricant application.²⁵ The specific gravities of both oils are relatively high, this is probably the result of the hydroxyl groups in their carboxylic chains. The acid value of castor seed oil is negligible when compared to that of HRSO. CSO has a lower saponification value than that of HRSO. This means that HRSO has a higher lauric acid composition than CSO. Both oils have an iodine value of less than 115 (gI₂/100 g), making them nondrying oils.¹⁵ The lower iodine value of HRSO shows that it has more oxidative stability than CSO. This is a very vital

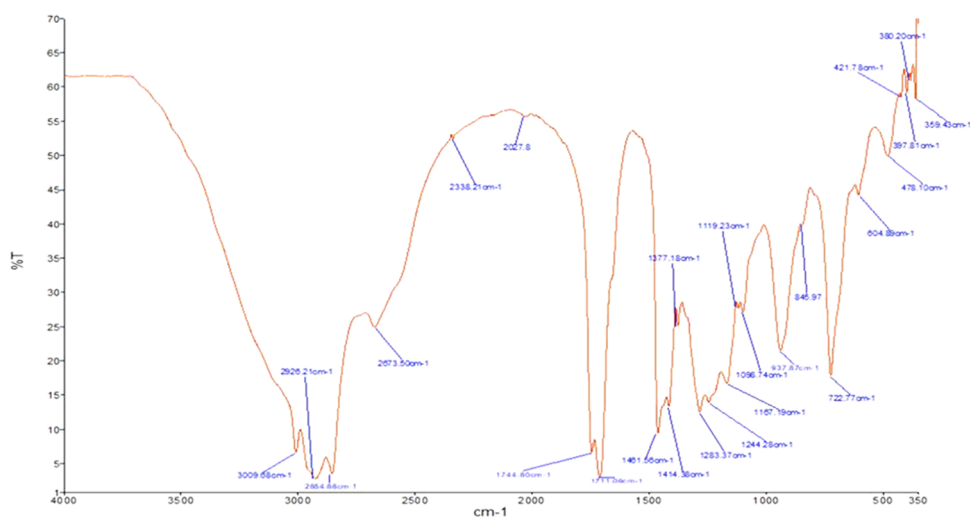


Figure 5. FTIR spectrum of rubber seed oil.

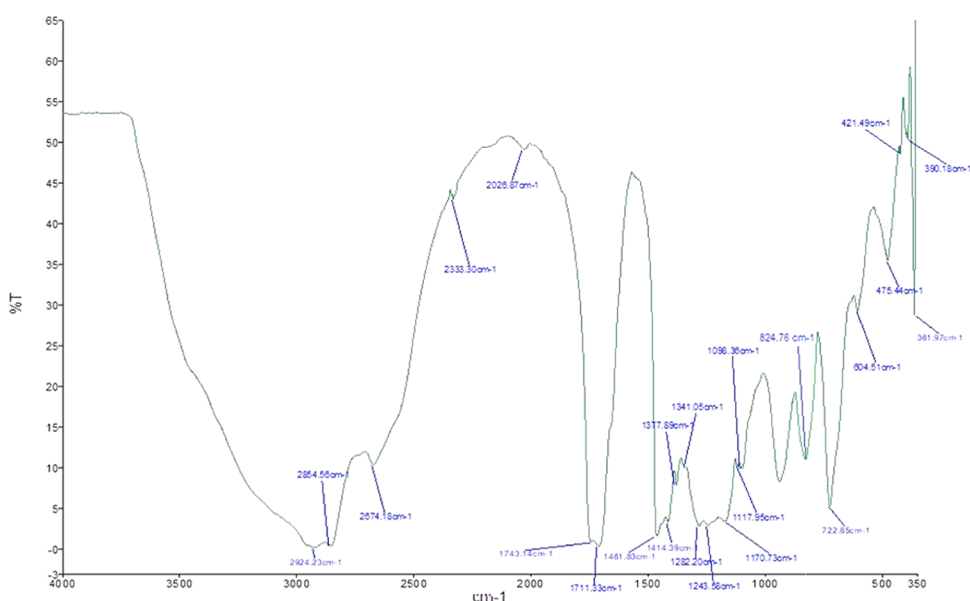


Figure 6. FTIR spectrum of ERSO.

attribute to consider when selecting a biodegradable base lubricant.^{9,12,13}

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 physicochemical findings also affirmed that HRSO could be synthesized by opening up the epoxy rings at optimal epoxide yield at a minimal temperature of $\geq 80\text{ }^{\circ}\text{C}$ 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.

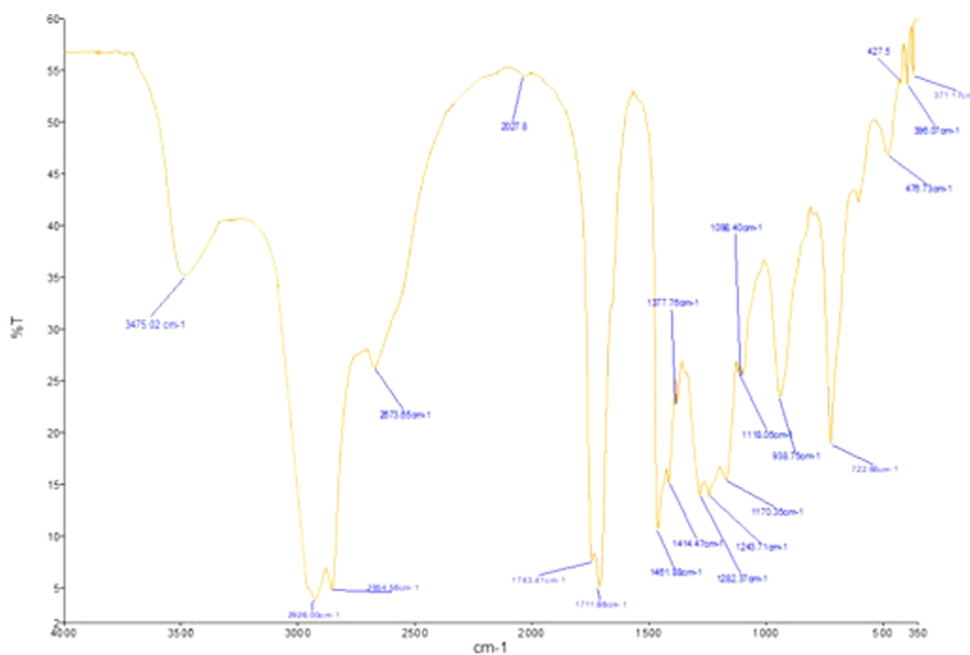


Figure 7. FTIR spectrum of HRSO.

Table 4. IR Peaks and Equivalent Functional Groups of RSO, ERSO, and HRSO

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

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

Table 5. Main IR Peaks and Their Conforming Functional Groups of CSO

frequency	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 synthesized HRSO, meaning there are fewer unsaturated bonds present in HRSO. Also, the higher viscosity index of

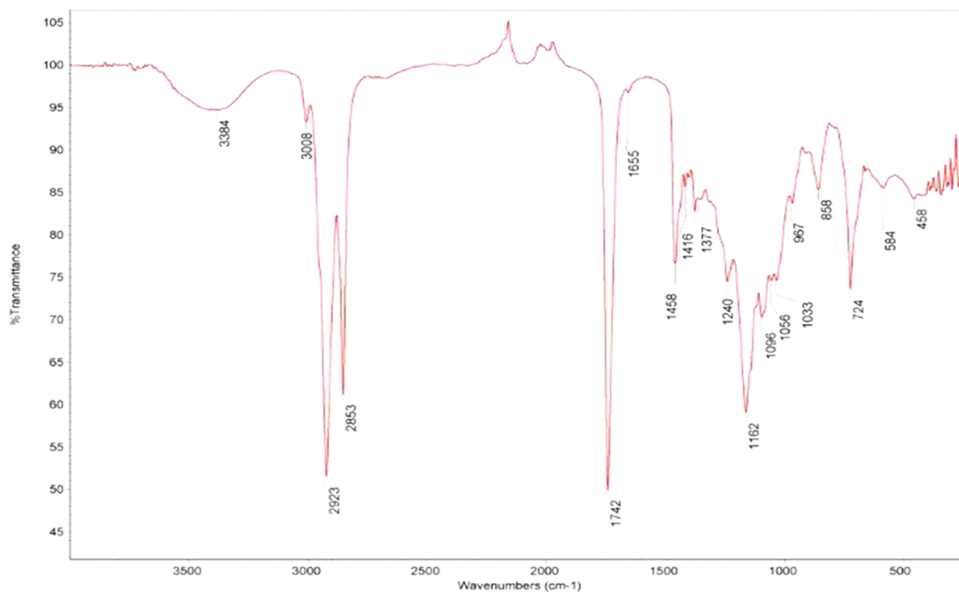


Figure 8. FTIR spectrum of castor oil (CSO).

HRSO compared to that of castor oil puts it in an advantageous position with regard to lubrication applications.

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Author Contributions

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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