ONE-POT-TWO-STEP SYNTHESIS OF BIOLUBRICANT BASE STOCK FROM RUBBER SEED OIL

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ABSTRACT

Biolubricant base stock was synthesized in this work from rubber seed oil in a one-pot-two-step process of epoxidation and hydroxylation. Rubber seed oil was extracted using a Soxhlet apparatus. The *in situ* epoxidation of the rubber seed oil with peracid (hydrogen peroxide and acetic acid) was analysed and optimized considering three process variables with their range of values given as temperature of 35-50 °C, time of 60-180 mins and mole ratio of hydrogen peroxide to acetic acid of 1:0.25-1:1 by applying the central composite design of response surface methodology. The ring opening reaction (hydroxylation) of the epoxide to polyhydroxylated oil (lubricant basestock) with ethanol was carried out using the optimum conditions obtained from the epoxidation process. The rubber seed oil, epoxide and lubricant basestock were characterized in terms of physico-chemical properties using standard methods and in terms of functional groups using Fourier Transform Infrared (FTIR) spectroscopy. Maximum epoxide content of 4.85% and maximum conversion of 71% of rubber seed oil to epoxide was achieved at a temperature of 50 °C, reaction time of 180 mins and 1: 0.39 mol/mol of hydrogen peroxide to acetic acid. The predicted values of the epoxidation process reasonably agreed with the experimental ones and model R-squared value of about 95% showed that response surface method can reasonably predict the epoxidation process using a quadratic polynomial model. There was 75% conversion of the epoxide to polyhydroxylated oil (biolubricant basestock), which represents a very high yield. The formation of epoxides and polyhydroxylated oil lead to modification (improvement) in the properties of rubber seed oil as confirmed by the physico-chemical properties and FTIR spectra analysis of the oil, epoxide and lubricant basestock. The study showed that chemical derivatives of rubber seed oils are an attractive, renewable, and ecofriendly alternative to mineral oils for lubricant formulations.

Keywords: Rubber seed oil, epoxidation, hydroxylation, response surface methodology

1.0 INTRODUCTION

Petroleum or mineral oil which currently serve as major base stocks for lubricant formulations are not environmental friendly coupled with difficulties for their safe and easy disposal. It is claimed that 50% of all lubricants sold worldwide end up in the environment via accidental spillage, non-recoverable usage, volatility, industrial and municipal waste, urban runoff, refinery processes and total loss applications (in chainsaw oils, two-stroke engines, concrete mold release oils, exhaust fumes in engines and metal cutting and forming processes) [1,2].

Plant-based oils are showing great potentials nowadays and are highly attractive material to replace the conventional mineral oils for use in lubricant production because they are structurally similar to the long chained hydrocarbons in mineral oils with the

characteristics of being renewable, non-toxic, economic and environmentally friendly [3,4]. In the past few decades, there have been environmental public awareness and any product that does not meet the environmental standard of biodegradability is considered dangerous to the environment.

Though most currently used lubricants originate from petroleum base stocks, vegetable oils have seen a promising increase in use as biodegradable fluids over the last decade. Environmental concerns as well as economics and performance issues will drive the market share for these oils [5]. Vegetable oils have very low volatility due to the high molecular weight of triglyceride structure and narrow range of viscosity change with temperature. Their ester linkages deliver inherent lubricity and are able to stick to metal surfaces. Further, vegetable oils have more superior solubilizing power for contaminants and additive

molecules than mineral-based fluids. Some performance limitations of vegetable oil base stocks in lubricant formulations are their poor oxidative stability, deposit-forming tendency, low temperature solidification and low-hydrolytic stability. On the other hand, parameters such as lubricity, antiwear protection, load-carrying capacity, rust prevention, foaming, and demulsibility are mostly additive-dependent [2]. Therefore, when a given vegetable oil is considered as a potential base stock for industrial or automotive application, the base-stock-dependent parameters must be evaluated first. The performance limitations of vegetable oil-based stocks can be overcome by genetic modification, chemical modification, processing changes, and development in their additive technology [5] such as esterification, epoxidation and hydrogenation [6].

A potentially very attractive plant oil for the synthesis of advanced materials is the oil from rubber seeds of the rubber tree (*Hevea brasiliensis*). So far, the tree has been cultivated mainly as an industrial crop for the production of natural rubber and valorization of the seeds has received limited attention. Rubber seed oil (RSO) is particularly attractive as it has a relatively high content of unsaturated fatty acids [7, 8], high amount of oil and does not compete with food oils [8].

Response surface methodology (RSM) can be used to evaluate the relative significance of several factors in the presence of complex interactions. RSM answers the question of how to select the levels for the applied factors to obtain the desirable, smallest or largest, value of the response function in a reduced number of experiments [9]. In this work, biolubricant base stock was synthesized by chemically modifying the properties of rubber seed oil via a two-step process of epoxidation and hydroxylation. RSM was employed in the epoxidation of rubber seed oil with peracids to determine the effect of epoxidation process parameters on the epoxide content.

2.0 MATERIALS AND METHODS

Already shelled rubber seeds were collected from Rubber Research Institute of Nigeria, Benin City, Nigeria. The kernels were dried, milled and stored for oil extraction and analysis. All reagents used in this work were of analytical grade and were used without further purification. The oil extraction was done following method by Nwabanne and Omoniyi [10]. The extraction process was carried out in a 2000 ml

Soxhlet extractor using n-hexane as solvent. n-hexane of 150 ml was poured into a 500 ml round bottom flask and 600 g of the milled kernels were placed in the thimble and inserted in the center of the extractor. The Soxhlet was heated at 60 °C (near the boiling point of n-hexane). As the solvent starts boiling, the vapour rose through the vertical tube into the condenser at the top. The liquid condensate dripped into the filter paper thimble in the center which contained the solid sample to be extracted. The extract seeped through the pores of thimble and filled the siphon tube, where it flowed back down into the round bottom flask. This was allowed to continue for 5min. At the end, the solvent was evaporated using a rotary evaporator and the percentage oil extracted was determined using the expression in Equation (1). The extraction process was repeated severally until the desired amount of the oil needed for further analysis was obtained.

$$\text{Percentage oil yield} = \frac{\text{mass of oil}}{\text{mass of seed}} \times 100\% \quad (1)$$

2.1 Epoxidation reaction and experimental design

The epoxidation reaction was carried out in a three-necked round bottom flask (250 ml capacity), equipped with a magnetic stirrer, a funnel and a thermometer and the setup was placed in a water bath. The center neck was connected to a reflux condenser and the thermometer was connected to another neck in order to record the reaction temperature that was controlled within ± 2 °C. Epoxidation method used was according to Goud *et al.* [11]. Mass of 25.8 g of rubber seed oil was placed in the reactor. The calculated amounts of acetic acid and sulphuric acid (catalyst) was added and stirred for 30 mins. Hydrogen peroxide was added to the mixture dropwise at a rate to ensure it was completed in half an hour. The completion of H₂O₂ addition was recorded as zero time and the epoxidation reaction was performed according to the experimental design of Table 1. The mixture in round bottom flask was stirred continuously to avoid zones of high peroxide concentration that could lead to explosive mixtures. After that, the collected samples were centrifuged before determining oxirane oxygen content.

RSM was used to assess the influence of various process parameters to maximize oxirane oxygen content (epoxide content). The experimental design for this reaction was carried out by employing a full factorial rotatable central composite design (RCCD) for three factors with replicates at the centre point and

star points were used in the investigation by the statistical software package Design-expert® (version 8.0.6; stat-ease, Inc., Minneapolis, USA). The variables used were temperature (x_1), time (x_2), and mole ratio of hydrogen peroxide to acetic acid (x_3), each at low (-1) and high (+1) coded levels. A total of 20 experimental trials that included 8 trials for factorial design, 6 trials for axial points (two for each variable) and 6 trials for replication of the central points were

performed. The response, relative conversion (Y) is the average of duplicate determination of oxirane oxygen content. The levels of independent variables were selected based on values obtained in preliminary experiments reported by Okieimen *et al.* [8]. Table 1 shows the CCD experimental range of values for the process variables considered for the epoxidation process.

Table 1: CCD experimental conditions for the epoxidation process

Independent variable	Symbol	Levels	
		-1	+1
Temperature (°C)	x_1	35	60
Time (mins)	x_2	60	180
HP:AA (mol/mol)	x_3	1:0.25	1:1

HP = Hydrogen peroxide AA = Acetic acid

The experimental data were analyzed according to the response surface regression procedure to fit the second-order polynomial equation as given by Equation (2) in which the level of significance (p-value) of all coefficients was < 0.05 . Based on experimental data shown in Table 1, the regression coefficient was determined to predict the process response as a function of independent variables and their interactions were used to understand the system behaviour.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^n \sum_{j>1}^n \beta_{ij} x_i x_j \quad (2)$$

where Y is the response, i.e. the relative conversion to oxirane oxygen (%), X_i and X_j represent the independent variables, β_0 is constant, β_i is linear term coefficient, β_{ii} is the quadratic term coefficient, β_{ij} is cross-term coefficient and 'n' is the number of process variables studied and optimized during the study. ANOVA was carried out to estimate the effects of process variables and their possible interaction effects on the maximum ethanol yield in the response surface regression procedure. The goodness and best fit of the model was evaluated by a regression coefficient R^2 . The response surface and contour plots were obtained using the fitted quadratic polynomial equation generated from regression analysis by keeping one of the independent variables at central value (0) and varying the other two. A direct Oxirane value indicates the mass of oxygen present in the epoxy groups. Experimentally, oxirane values were determined by the direct method using hydrobromic acid solution in

glacial acetic acid [11]. Theoretical oxirane oxygen (OO_{the}) and the relative percentage conversion to oxirane were computed from the following expressions:

$$OO_{the} = \left[\frac{(IV_0/2A_i)}{100+(IV_0/2A_i)A_0} \right] A_0 \times 100\% \quad (3)$$

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

$$Relative\ conversion\ (\%) = \left[\frac{OO_{exp}}{OO_{the}} \right] \times 100\% \quad (4)$$

Where OO_{exp} is the experimentally determined content of oxirane oxygen in 100 g of oil, and OO_{the} is the theoretically maximum oxirane oxygen content in 100 g of oil [12]. Each oxirane oxygen content analysis was duplicated, and the average values were reported.

2.2 Hydroxylation of the epoxide (Ring opening reaction)

The ring-opening reaction was carried out in similar set up as the epoxidation process. This hydroxylation reaction of the epoxide to open its ring was performed following optimal conditions reported by Tucor *et al.* [13] with modification in the type of catalyst used and reaction time. For the hydroxylation step, 2 wt% of H_2SO_4 (catalyst) was used in the ring-opening reaction for 4 hr at a temperature of 80 °C using 10:1 mole of

ethanol to epoxidised rubber seed oil (ERSO). The ethanol and catalyst were mixed and heated to 80 °C, then ERSO was added to start the reaction process. Samples were withdrawn after the reaction time, quenched and centrifuged to separate the solid catalyst. The residual solvent was then evaporated by heating at 80 °C under high vacuum. The product of the hydroxylation process is known as polyhydroxylated oil or hydroxylated rubber seed oil (HRSO).

The oxirane conversion to HRSO was calculated using Equation (5) as:

$$\text{Oxirane conversion} = \frac{(ON_i - ON_f)}{ON_i} \quad (5)$$

where ON_i and ON_f are the initial and final oxirane numbers, respectively.

2.3 Characterization of RSO, ERSO and HRSO

RSO, ERSO and HRSO were characterized in terms of physico-chemical properties using standard methods and in terms of functional groups using FTIR analysis using a Perkin Elmer Spectrum (ASC III PEDS 1.60). The samples were used in the form of potassium bromide (KBR) discs which were prepared by grinding 1 mg sample/100 mg pre-dried KBR. The spectra were recorded in the range of 4400-350 cm^{-1} .

3.0 RESULTS AND DISCUSSION

3.1 Analysis of epoxide yield

Oil yield of 43.68% was obtained after extraction with 150ml of 99.5% n-hexane. This amount of oil was extracted from 600 g of the rubber seed kernel using Soxhlet apparatus. This amount represents a high yield of oil and is in accordance with the range of 35 – 45% RSO yield reported by Nwokolo *et al.* [14]. The iodine value of the RSO was found to be 117.0 g. I_2 /100g and the theoretical yield of oxirane oxygen was calculated to be 6.869% using Equation (3). The epoxide content was determined from 0.05 mol of RSO and 1.00 mol (34.01 g) of hydrogen peroxide which was fixed all epoxidation experimental runs varying only the number of moles of acetic acid. Table 2 gives the experimental matrix and epoxide content obtained after epoxidation of RSO with per acid. The maximum observed relative conversion of RSO to epoxide content was 70.90% while the lowest was 6.48%. The maximum relative conversion was obtained at a temperature of 50 °C, time of 180 mins and 0.25 mol of

acetic acid (AA). The predicted vs. actual plot for the relative conversion of RSO to epoxide is given by Figure 1 which showed a strong linear correlation between the predicted and the actual values, which indicate model is satisfactory. Table 3 gives the analysis of variance (ANOVA) of the relative conversion of RSO to epoxide. P-values less than 0.05 indicate model terms/factors are significant i.e. change in the factor leads to a corresponding change in relative conversion of RSO to oxirane oxygen at a significant level of 5%. From Table 3, high F-value of 32.32 and very low p-value of <0.0001 (<0.05) indicate model is highly significant. Among the main/linear factors, temperature (x_1) and time (x_2) are highly significant while variation in the molar ratio of hydrogen peroxide to acetic acid (x_3) is insignificant on the relative conversion of RSO to ERSO. Only the interaction of time and mole of acetic acid (x_2x_3) were found to be significant among the interaction factors, while all quadratic factors (x_1^2, x_2^2 , and x_3^2) were significant model terms. There is insignificant lack of fit with p-value of 0.0670 which shows the quadratic model reasonably predicted the epoxidation process. Equation (6) gives the empirical model of the epoxidation process, showing the relationship between relative conversion of RSO to ERSO and the variables considered (significant only) in coded values.

$$Y (\%) = 63.09 + 7.40x_1 + 7.57x_2 + 0.58x_3 - 18.27x_2x_3 - 4.81x_1^2 - 6.62 - 17.45x_3^2 \quad (6)$$

In a regression equation, when an independent variable has a positive sign, it means that an increase in the variable will cause an increase in the response while a negative sign will result in a decrease in the response [15,16] Hence, an increase in temperature (x_1), time (x_2) and molar ratio of hydrogen peroxide to acetic acid (x_3) will lead to an increase in the relative conversion of RSO to OO. Epoxidation time (x_2) showed the highest significant effect on the relative conversion to ERSO while mole of acetic acid showed the least effect among the main/linear variables. The coefficient of regression R^2 was used to validate the fitness of the model equation. Table 4 gives an R^2 of a high value of 0.9496, showing that 94.96% of the variability in the relative conversion of the process can be explained by the model. There is also positive significant correlation between the adjusted R-squared value (0.9131) and the predicted R-squared value (0.6477), which shows that the model reasonably

predicted the epoxidation process using a quadratic polynomial.

Figure 1: Predicted vs. actual plot for the relative conversion of RSO to epoxide

Table 2: Experimental design matrix with relative conversion to oxirane oxygen

Std order	Coded factors			Actual factors			Y (%)	
	x_1	x_2	x_3	$x_1 = temp.$	$x_2 = time$	$x_3 = mol (AA)$	Actual	Predicted
1	-1	-1	-1	35	60	0.25	6.48	0.40
2	1	-1	-1	50	60	0.25	19.01	15.19
3	-1	1	-1	35	180	0.25	53.42	52.06
4	1	1	-1	50	180	0.25	70.90	66.86
5	-1	-1	1	35	60	1.00	44.12	38.09
6	1	-1	1	50	60	1.00	56.44	52.88
7	-1	1	1	35	180	1.00	26.39	16.69
8	1	1	1	50	180	1.00	26.87	31.49
9	-1.68	0	0	29.89	120	0.625	26.88	37.05
10	1.68	0	0	55.11	120	0.625	61.5	61.93
11	0	-1.68	0	42.5	19.09	0.625	23.66	31.64
12	0	1.68	0	42.5	220.91	0.625	54.47	57.09
13	0	0	-1.68	42.5	120	0.01	9.48	15.20
14	0	0	1.68	42.5	120	1.25	10.32	15.57
15	0	0	0	42.5	120	0.625	63.16	63.09
16	0	0	0	42.5	120	0.625	63.43	63.09
17	0	0	0	42.5	120	0.625	63.06	63.09
18	0	0	0	42.5	120	0.625	63.23	63.09
19	0	0	0	42.5	120	0.625	63.41	63.09
20	0	0	0	42.5	120	0.625	63.36	63.09

Table 3: ANOVA of the relative conversion of RSO to epoxide

Source	Sum of squares	Df	Mean square	F Value	p-value Prob > F
Model	8850.0302	7	1264.2900	32.3236	< 0.0001*
x_1 -temperature	747.4490	1	747.4490	19.1097	0.0009*
x_2 -time	782.0544	1	782.0544	19.9945	0.0008*
x_3 -no. of moles (AA)	4.5136	1	4.5136	0.1154	0.7400
x_2x_3	2669.2471	1	2669.2471	68.2436	< 0.0001*
x_1^2	333.9367	1	333.9367	8.5376	0.0128*
x_2^2	632.8917	1	632.8917	16.1809	0.0017*
x_3^2	4163.1043	1	4163.1043	106.4364	< 0.0001*
Residual	469.3625	12	39.1135		
Lack of fit	469.3625	7	67.0518	6.2289	0.0670
Pure error	53.823	5	10.7646		
Cor. Total	9319.3927	19			

*=significant

Table 4: Model summary statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	22.0630	0.1643	0.0076	-0.3518	12597.530	
2FI	19.7605	0.4553	0.2039	-0.0190	9496.784	
Quadratic	6.5300	0.9496	0.9131	0.6477	3283.118	Suggested
Cubic	0	1	1		+	Aliased

Figure 2 (a) gives the response surface plot showing the interaction effect of epoxidation time and mole acetic acid on the relative conversion of RSO to

epoxide while Figure 2 (b) gives the corresponding contour plot.

(a)

(b)

Figure 2.(a) Response surface plot (b) corresponding contour plot showing the interaction effect of epoxidation time and mole of acetic acid (AA).

The relationship between independent and dependent variables is illustrated in three dimensional representation of the response surfaces as by Figure 2 (a) and two-dimensional contour plots, Figure 2 (b) generated by the model gives the effect of interaction of time (60-180 mins) and mol/mol hydrogen peroxide to acetic acid (0.25-1.00) on the relative conversion of RSO to epoxide at constant temperature. As both epoxidation time and mole of AA increased the relative conversion of RSO to OO also increased. The achieved maximum desirability of 0.984 means that it is possible to reach maximum relative conversion target. The maximum oxirane oxygen of 4.85% and maximum

relative conversion of the epoxidation process of 70.90% was obtained at a temperature of 50 °C, time of 180 mins and 0.39 mol/mol hydrogen peroxide to acetic acid.

3.2 Physico-chemical properties

The ring opening reaction (hydroxylation) of the epoxide gave a polyhydroxylated oil with the following physico-chemical properties. The esterification process gave the desired biolubricant basestock (ester derivative) with 75% conversion of epoxide to HRSO (biolubricant base stock). Table 5 gives the physico-chemical properties of RSO, ERSO and HRSO.

Table 5: Physico-chemical properties of HRSO, ERSO and RSO

Properties	RSO	ERSO	HRSO
Colour	Yellow	Yellow	Yellow
Acid value (mgKOH.g ⁻¹)	39.97	34.70	32.50
Saponification value (mg KOH/g)	204.84	215.86	232.12
Specific gravity @ 30°C	0.912	1.031	1.001
Viscosity @ 30°C (cp)	60.90	161.50	166.57
Refractive index (°)	1.4709	1.4690	1.4405
Iodine value (g I ₂ . [100 g] ⁻¹)	117.00	17.12	9.88
Epoxide content (%)	-	4.85	1.41

Figure 3 (a), (b) and (c) gives the FTIR spectra of RSO, ERSO and HRSO respectively. There are similarities in the FTIR spectra of HRSO, ERSO and RSO as depicted by the Figures. The difference in the spectra for RSO and ERSO is that ERSO shows absorption at 864.33 cm⁻¹. Okieimen *et al.* [17] reported this difference by absorption at 824 cm⁻¹ which denote the presence of epoxide while Gamage *et al.* [18] reported the presence of epoxide after epoxidation of waste cooking oil at 838.00 cm⁻¹. Farias *et al.* [19] identified that via oxirane ring opening reaction, OH functional groups can be derived from epoxy functional groups. In this study, FTIR spectra

exhibited no trace of OH absorption peak at approximately 3000–3300 cm⁻¹ as shown by the spectra in Figure 3 (b) which represents no oxirane cleavage during the epoxidation reaction. This range of no oxirane cleavage was reported to be 3000 to 3500 cm⁻¹ for epoxidized waste cooking oil as reported by Gamage *et al.* [18]. The presence of OH at 3369.0 cm⁻¹ showed oxirane cleavage. This must have been due to epoxy ring opening to form hydroxylated product which resulted in a sharp and strong O-H stretching node at about 3418.00 cm⁻¹ in the IR spectrum of hydroxylated oil shown in Figure 3(c).

Figure 3. FTIR spectra of (a) RSO (b) ERSO and (c) HRSO

4.0 CONCLUSION

In this work, biolubricant basestock was synthesized from rubber seed oil by a one-pot-two-step process of epoxidation and hydroxylation. The epoxidation process was designed by varying temperature, time and mole ratio of hydrogen peroxide to acetic acid and the relative conversion of rubber seed oil to epoxide was designed, analyzed and optimized employing the central composite design of response surface methodology. Soxhlet apparatus gave 43.6% of rubber seed oil which represents a very high yield of oil from the kernel. Maximum epoxide content of 4.85% and maximum relative conversion of 71% to epoxide of the rubber seed oil was achieved at a temperature of 50 °C, reaction time of 3 hrs and 0.39 mol of acetic acid. There was 75% conversion of the epoxide to polyhydroxylated oil (biolubricant basestock), which represent a very high yield. The predicted values correlated reasonably with experimental values and high R-squared value of over 96% showed that response surface method can reasonably predict the process using a quadratic polynomial model. The formation of epoxides and polyhydroxylated oil lead to modification (improvement) in the properties of rubber seed oil as confirmed by the physico-chemical properties and FTIR spectra analysis of the oil, epoxide and polyhydroxylated oil. This study shows that chemical derivatives of rubber seed oil are an attractive, renewable, and ecofriendly alternative for mineral oils for the synthesis of lubricant formulations.

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