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OPTIMIZATION OF THE EPOXIDATION PROCESS PARAMETERS OF HURACREPITAN SEED OIL

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Abstract: This study was aimed at optimizing the key process parameters for the epoxidation of huracrepitan seed oil using Response surface methodology (RSM). Pure huracrepitan seed oil was epoxidized via in situ conventional method using hydrogen peroxide and acetic acid in the presence of sulfuric acid as catalyst. Box Behnken Design was used to analyze the effect of four variables, temperature (55-65°C), time (4-6 hours), stirring speed (1100-1300 rpm), and catalyst concentration (1-3 mol) on the percentage of oxirane produced from the epoxidized oil. Optimization of the effect of process parameters such as time, temperature, and catalyst concentration was studied. The optimal condition for the predicted oxirane value at 4.07169%, was obtained at a temperature of 66.18°C, a reaction time of 5.72 hours, stirring speed of 1184.16rpm and catalyst concentration of 2.35 mol. The resultant epoxide product was confirmed using Fourier transform infrared spectroscopy (FTIR) (at 1722.49 cm^{-1}).
Keywords: Huracrepitan seed oil, Optimization, Catalyst, Response Surface Methodology, oxirane value

1. INTRODUCTION

Since petroleum resources are ultimately limited, polymers based on plant seed oils are of great interest due to its environmentally friendly characteristics, biodegradability, and its renewable qualities [1]. There has consequently triggered the demand for more oils needed to expand the present supplies in the chemical industry. However, the current popular seeds have not been sufficient for the local food market. Although over the last decade a lot of seed oils have been characterized giving valuable information about their physio-chemical properties and chemical composition, most are still largely under-utilized. Hence, has been recommended by various researchers as popular raw material for industrial production and other products of modified vegetable oils [2-4]

Huracrepitan (sandbox tree) is a perennial crop of the family Euphorbiaceae. It is one of the tropical crops grown in North and South America, also common to Africa especially Nigeria where it is abundant [5]. Oil extracted from its seeds contains a volatile colourless liquid called "Hurin", though a vegetable oil, it is poisonous if ingested, hence the oil remains underutilized. Muhammed et al. [6] analyzed the fatty acid composition (wt%) of huracrepitan seed oils, from the assessment, it indicates that the oil contains unsaturated fatty acids via its oleic, linoleic and linolenic content as shown in Table 1.

Table 1: Fatty acid composition (wt%) of hura crepitan seed oils

Fatty acid	Hura crepitans
16:0	12.20+_0,20
16:1	0.10+_0.00
18:0	5.1+_0.30
18:1	27.2+_0.20
18:2	52.8+_0.10
18:3	1.8+_0.10
20:0	0.2+_0.10
20:1	0.3+_0.10
22:0	0.3+_0.10
Unsaturated	82.2+_0.20
Saturated	17.80+_0.20

Vegetable oils containing unsaturated fatty acids that have two or more double bonds between the two carbon atoms can be suitably epoxidized and further modified to biobased resins. These C=C bonds are the reactive sites for the modifications [7]. Studies have revealed that rubber seed oil, soya bean oil, sesame seed oil, and groundnut seed oil containing high unsaturated fatty acid triglycerides can be modified through several chemical processes [8-10].

In the chemical industry, epoxidation remains the most common value-adding modification to vegetable oil [11]. Epoxidation of fatty acids is a process of adding a single atom of oxygen to each unsaturated fatty acid chain (C=C) using oxidizing agents (peracid) to convert the unsaturated fatty acid chain into an epoxy group. [12]. Industrial methods usually involve the reaction of these unsaturated C=C double bonds with a peracid (that is, an acid with additional oxygen). This acid is formed by the reaction of an ordinary carboxylic acid (e.g. acetic acid) with hydrogen peroxide. The epoxides formed can be used as raw materials to synthesize cross-linkable bio-resins.

The epoxides obtained from triglycerides of unsaturated fatty acids are intermediates for a large number of various applications, such as stabilizers and plasticizers in polymers, additives in lubricants, polyols in polyurethane foam. [13-16]. Recent studies have attempted to improve epoxidation effectiveness under milder

conditions that minimize by-product formation, reaction time, and optimize the process parameters to obtain the desired epoxide [17]. Optimization of the process parameter of some vegetable oils like canola, soya bean, rapeseed, and sesame seed oil has been investigated by [18-21] respectively. Hence this work investigates the optimum epoxidation condition for huracrepitan seed oil varying the process parameters such as time, stirring speed, catalyst concentration, and temperature.

2. MATERIALS AND METHOD

— Materials

Pure rubber seed oil obtained from Integrated Rubber Products Nigeria Plc, acetic acid (85%), hydrogen peroxide (30wt%). sodium carbonate was procured from Vinod Chemical Industries, Aba, Nigeria.

— Equipment

Magnetic heater, three-necked round bottom flask, thermometer, condenser, feed funnel, stirring bulb, measuring cylinder, weighing balance, separation funnel, rotary evaporator.

— Design of Experiment

The experiment was designed with Box Behnken considering 4 factors (temperature, time, stirring speed, and catalyst concentration) and 1 response (oxirane value) comprising of 29 experimental runs using Design Expert Software version 6.0.8.

Table 2: Independence factors and their coded value levels

				level		
Factors	Name	Unit	Type	-1	0	1
A	Temperature	°C	Numeric	55	60	65
B	Time	Hours	Numeric	4	5	6
C	Stirring speed	Rpm	numeric	900	1100	1300
D	Catalyst concentration	Mol	Numeric	1	2	3

— Epoxidation procedure

The epoxidation method reported by Goud et al. [22] was used with little variation in procedure, and this was repeated for all the experimental runs with the same concentration but different reaction times. 30ml of huracrepitan seed oil was placed in the flask, 15ml of acetic acid and H_2SO_4 as a catalyst was added to the flask after about five minutes, the mixture was stirred continuously for 30 minutes. Then (45ml) of 30wt% aqueous hydrogen peroxide was added dropwise to the reaction mixture, as oxygen donor, at a rate such that the hydrogen peroxide addition was completed within half an hour; The mole ratio of the components used was 1:1.5:0.5, (H_2O_2: CH_3COOH). After the complete addition of hydrogen peroxide, the mixture was heated under reflux at a temperature in accordance to design and with rapid stirring. The rapid stirring was maintained throughout the experiment to achieve fine dispersion of oil and to avoid zones of high peroxide concentration. The collected samples of the Epoxidised Rubber seed oil (ERSO) were washed with sodium carbonate (Na_2CO_3) which was dissolved in distilled water to remove the free acids and other unreacted components. 10g of Na_2C0_3 was first dissolved in 100ml of distilled water. Then, another 100ml of distilled water was further added to the mixture. The total mixture was added to the sample and separated by a separating funnel. Subsequent extraction was used to recover the remaining samples after washing

— Analytical techniques

≡ Oxirane Oxygen content

The percentage of the oxirane oxygen was determined by a direct method established by using a hydrobromic acid solution in glacial acetic acid. The oxirane oxygen (OO) content was calculated according to the consumed amount of the halogen atom.

The Oxirane Oxygen Content of the analyzed samples was calculated using the formula:

$$OV = \frac{(B-S)\times M\times A_o\times 100}{1000W} \quad (1)$$

where: S = Volume of NaOH used for sample (ml), B = Volume of NaOH used for blank (ml), M = Molarity of the NaOH used, W = Weight of sample used (g), A_o = Atomic weight of oxygen

≡ FT-IR analysis

Fourier Transform Infrared (FT-IR) Spectroscopy analysis was carried out to verify the functionalization of the rubber seed oil.

3. RESULTS AND DISCUSSION

— Statistical analysis of data for epoxidation of huracrepitan seed oil

The results of the oxirane value presented in Table 3 were determined using Equations 1, respectively... The statistical analysis for epoxidation of huracrepitan seed oil was done using an analysis of variance (ANOVA). Table 4 shows the ANOVA results for huracrepitan seed oil epoxidation for oxirane value respectively. The multiple regression analysis of the experimental data gives a second-order polynomial equation. The quadratic

model developed depicts the interaction between the oxirane value (Y) and the coded values of the independent variables A, B, C, and D (temperature, time, stirring speed, and catalyst concentration).

$$Y = 1.52 + 0.15A + 0.62B + 0.42C - 0.32D - 0.10A^2 + 0.67B^2 + 0.38C^2 - 0.35D^2 + 1.65AB + 1.24AC - 0.21AD - 0.83BC + 2.00BD - 0.093\,CD \quad (2)$$

where Y represents response variable oxirane value measured in %.

Table 3: Experimental design

Runs	A Temperature (oC)	B: time (h)	C: Stirring speed(rpm)	D:Catalyst conc. (mol)	Response: Oxiraine value
1	55	5	1100	1	1
2	60	4	1300	2	3.28
3	60	4	900	2	0.56
4	60	6	1300	2	3.01
5	55	4	1100	2	3.01
6	55	6	1100	2	0.89
7	55	5	1100	3	1
8	60	5	900	1	1.54
9	65	5	1100	3	0.8
10	65	5	900	2	0.32
11	60	5	900	3	0.88
12	60	5	1100	2	1.52
13	60	4	1100	1	0.6
14	60	6	1100	3	4.08
15	60	5	1100	2	1.52
16	65	6	1100	2	4.44
17	65	5	1100	1	1.66
18	65	5	1300	2	2.4
19	60	5	1300	1	3.3
20	60	5	1300	3	1.35
21	65	4	1100	2	2.1
22	55	5	900	2	2.4
23	60	4	1100	3	2.7
24	60	5	1100	2	1.52
25	55	5	1300	2	0.72
26	60	5	1100	2	1.52
27	60	6	900	2	2.7
28	60	6	1100	1	0.72
29	60	5	1100	2	1.52

Table 4: Analysis of variance (ANOVA) results for response surface quadratic model of oxirane value

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	27.9	14	1.99	65.23	< 0.0001	Significant
A	0.16	1	0.16	5.24	0.0513	
B	2.03	1	2.03	66.6	< 0.0001	
C	1.07	1	1.07	34.93	0.0004	
D	0.59	1	0.59	19.28	0.0023	
A^2	0.049	1	0.049	1.61	0.2399	
B^2	1.79	1	1.79	58.47	< 0.0001	
C^2	0.59	1	0.59	19.29	0.0023	
D^2	0.54	1	0.54	17.68	0.003	
AB	6.14	1	6.14	200.86	< 0.0001	
AC	3.53	1	3.53	115.53	< 0.0001	
AD	0.18	1	0.18	6.05	0.0393	
BC	1.66	1	1.66	54.36	< 0.0001	
BD	5.94	1	5.94	194.4	< 0.0001	
CD	0.02	1	0.02	0.64	0.4453	
Residual	0.24	8	0.031			
Lack of Fit	0.24	4	0.061			Not significant
Pure Error	0	4	0			
Cor Total	28.14	22				
Std. Dev.	0.17		R-Squared	0.9913		
Mean	1.71		Adj R-Squared	0.9761		
C.V.	10.24		Pred R-Squared	0.7799		
PRESS	6.19		Adeq Precision	29.956		

— Adequacy of the model

The significance and adequacy of the model were tested using ANOVA. It was observed from table 4, that all the coded factors are significant except (A, A^2, and CD), The greater the F-value, the more certain it is that the model explains adequately the variation in the data and the estimated significant terms of the epoxidation parameter variables are closer to the actual value. [23,24] The fitness of the polynomial model was expressed by the coefficient of determination (R^2) and the coefficient of adjusted R^2 and predicted R^2 which were obtained as 0.9913,0.9761 and 0.7799 respectively, it is an indication that the regression model is acceptable. The lack of fit value of 0.24 depicts non-significance, this implies pure error and low for the model, it shows

the adequate representation of the interaction by the model. Non-significant lack of fit of the model is good as the model could be used for theoretical prediction of the oxirane value, the adequate precision is greater than 4 which indicates that the model is strong enough to be used for optimization. The coefficient of variation (CV = 10.34%) was slightly greater than 10% which indicated a high degree of precision and reliability of the model.

Table 5: ANOVA analysis of experimental errors and confidence intervals for oxirane value

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1.52	1	0.078	1.34	1.7	
A-temperature	0.15	1	0.064	-1.023E-003	0.29	1.32
B-time	0.62	1	0.077	0.45	0.8	1.5
C-stirring speed	0.42	1	0.071	0.26	0.58	1.48
D-catalyst conc.	-0.32	1	0.073	-0.49	-0.15	1.55
A2	-0.1	1	0.081	-0.29	0.084	1.22
B2	0.67	1	0.088	0.47	0.87	1.31
C2	0.38	1	0.086	0.18	0.57	1.32
D2	-0.35	1	0.083	-0.54	-0.16	1.22
AB	1.65	1	0.12	1.38	1.92	1.31
AC	1.24	1	0.12	0.97	1.51	1.29
AD	-0.21	1	0.087	-0.42	-0.013	1
BC	-0.83	1	0.11	-1.09	-0.57	1.22
BD	2	1	0.14	1.67	2.33	1.35
CD	-0.093	1	0.12	-0.36	0.17	1.31

Table 5 shows an assessment of experimental errors and the confidence interval of the experimental variables indicating that the overall model for both responses is significant.

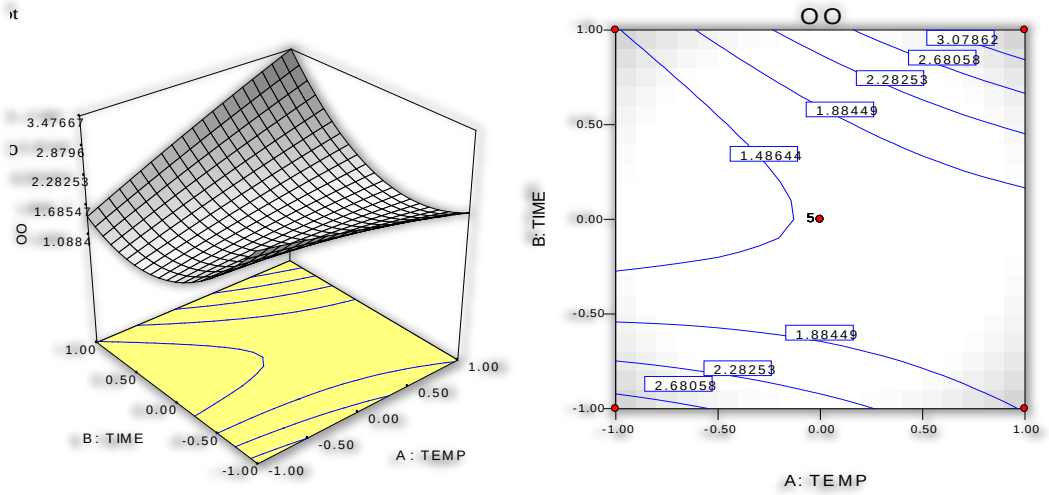

Figure 1: 3D and contour plot on the effect of time and temperature on oxirane value

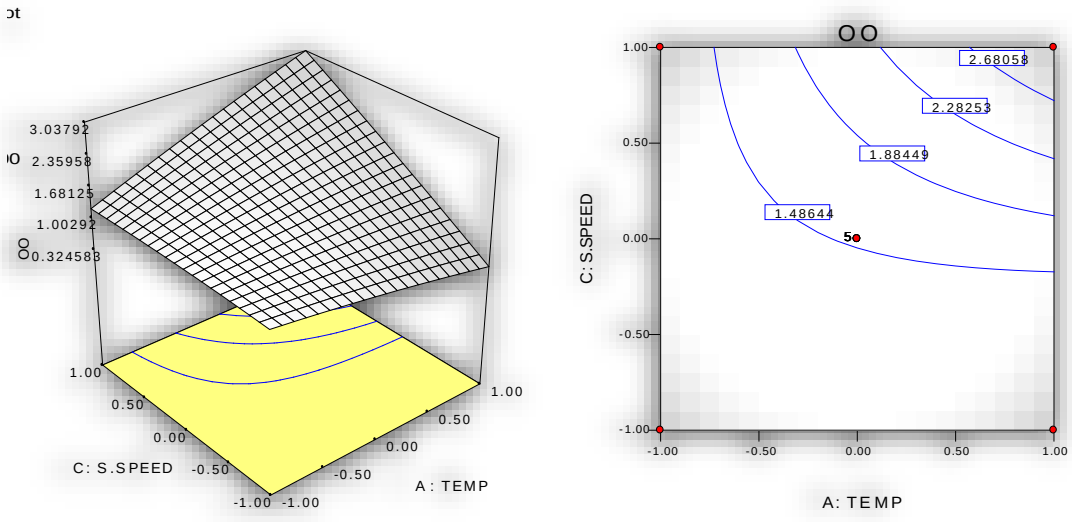

Figure 2: 3D and contour plot on the effect of stirring speed and temperature on oxirane value

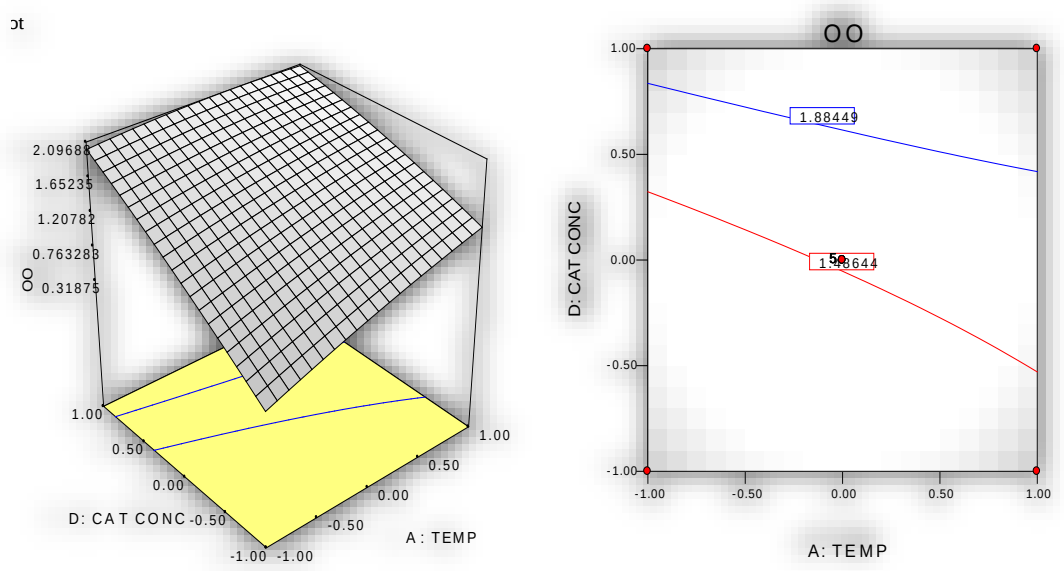

Figure 3: 3D and contour plot on the effect of catalyst concentration and temperature on oxirane value

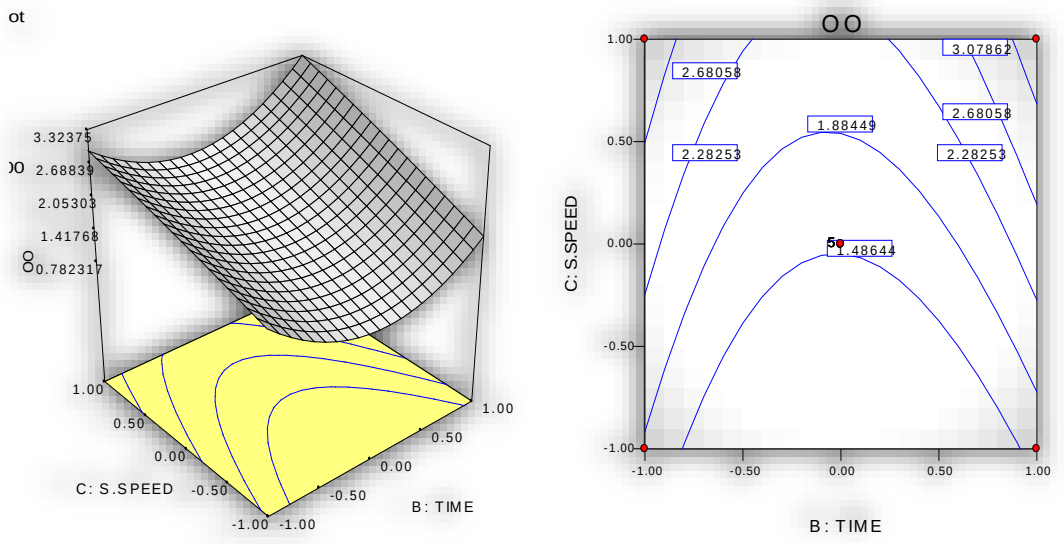

Figure 4: 3D and contour plot on the effect of stirring speed and time on oxirane value

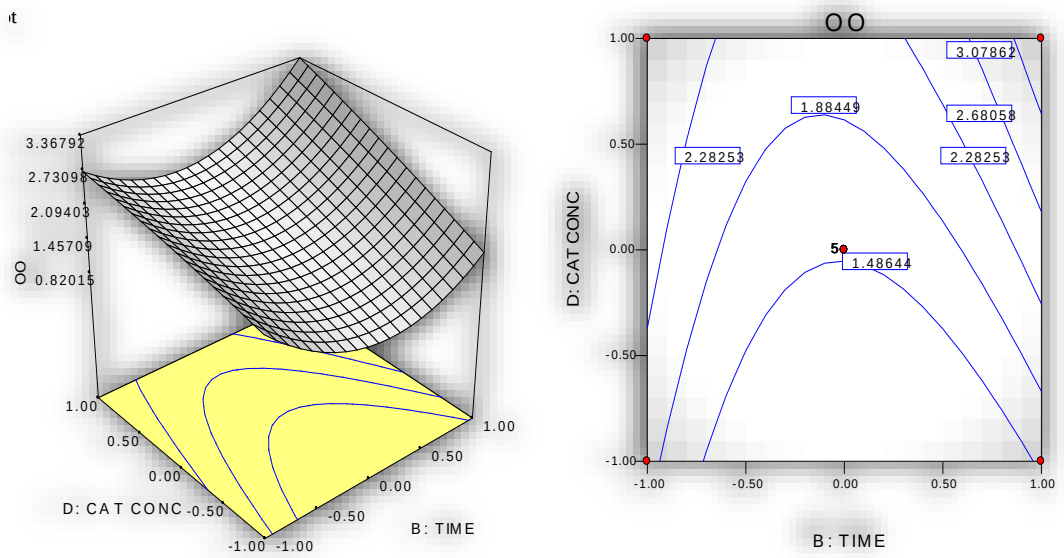

Figure 5: 3D and contour plots on the effect of catalyst concentration and time on oxirane value

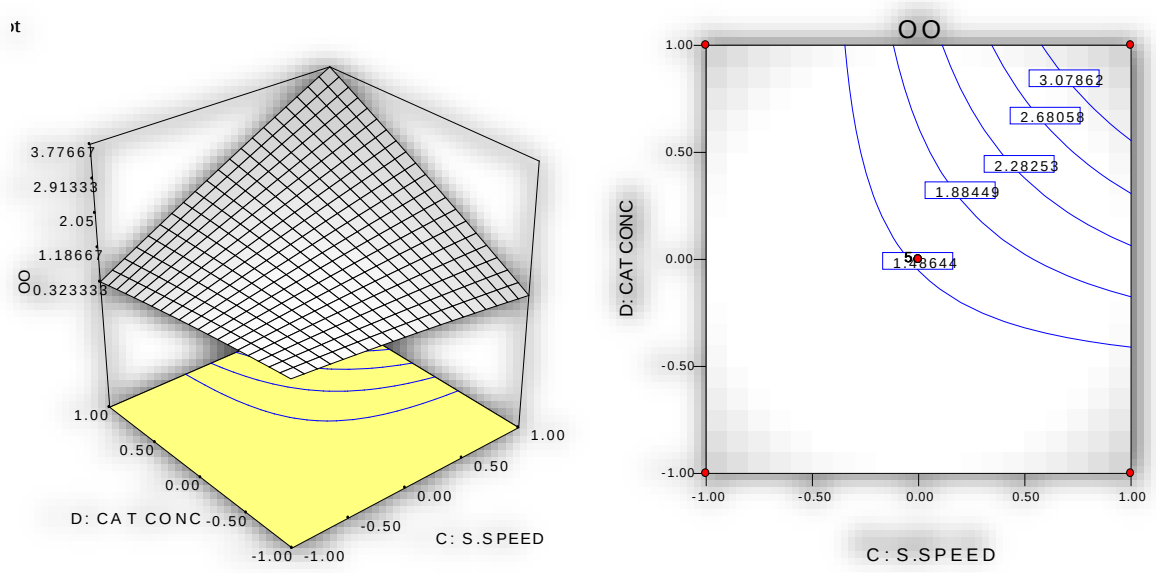

Figure 6: 3D and contour plot on the effect of catalyst concentration and stirring speed on oxirane value

The 3D response surface plots are the graphical representation of the regression equations used to visualize the relationship between the responses and experimental levels of each factor. The variation in oxirane value is displayed on the z-axis showing the three-dimensional relationship with factor variables on y and x-axis respectively. The interactions of the two factors are reflected in the contour of the plots. Rounded contour line indicates that a weak interaction of two factors and a distorted contour indicates a significant interaction of two factors [25], the effect of catalyst concentration and temperature on the oxirane value displayed a distorted contour, which indicates that the interaction between the factors is significant.

Normalization plots help in ascertaining if the models are satisfactory. The data were plotted against a theoretical normal distribution in such a way that the points should form an approximately straight line and a departure from this line would indicate a departure from a normal distribution., some data fell out of line, the ones distributed along the 45-degree line is enough to validate the model [26].

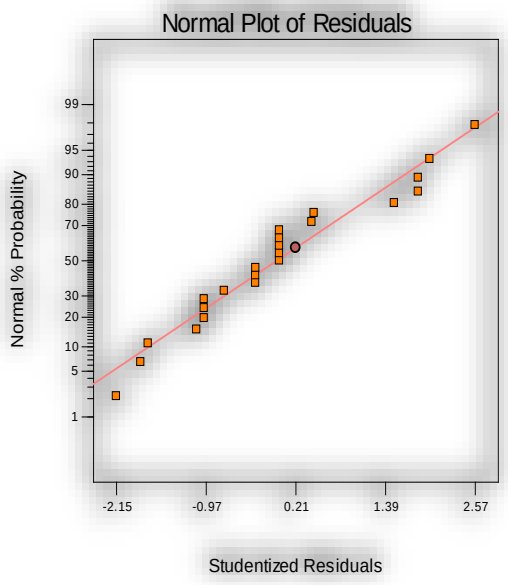

Figure 7: Normalization plots for oxirane value

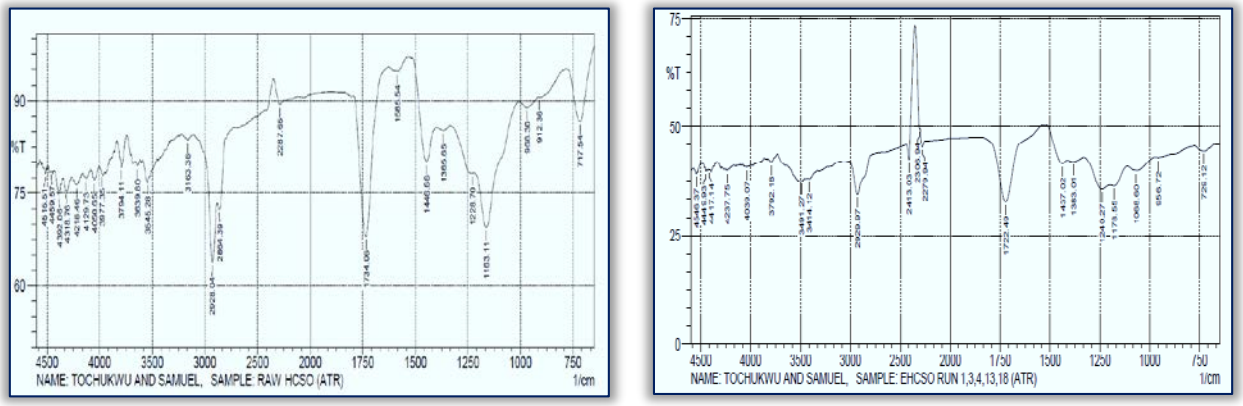

Figure 8: (a) FT-IR Results for Pure Huracrepitan Seed Oil (b) Epoxidized Hura Crepitan Seed Oil

In the FT-IR spectra, it can be seen that the presence of carbon-carbon double bonds (C=C) in the untreated rubber seed oil was indicated by the appearance of peaks at 1734.06cm^{-1}. The absorption band for the epoxy group in the HCSO was indicated by the single peak at 1722.49cm^{-1}, this peak was missing in the untreated oil. Hence, a pointer to the fact that the oil has been suitably epoxidized

— Optimization of epoxidation conditions

The conditions selected for optimization of the epoxidation of huracrepitan seed oil were temperature from 55 to 65^{0}C, time from 4 to 6hours, stirring speed from 900 to 1300 rpm, and catalyst concentration of 1 to 3mol. Optimization was done using desirability function, and desirability of 1 was obtained. The values of epoxidation parameters at optimum condition were a temperature of 64.18^{o}C, a time of 5.72 hours, a stirring speed of 1184.16rpm, and a catalyst concentration of 2.35 mol. The corresponding value of oxirane is 4.07169%.

4. CONCLUSIONS

The development of epoxidized huracrepitan seed oil was demonstrated and the formation of epoxy groups was confirmed by FTIR spectroscopy analysis. The optimal condition for the oxirane value is the time of 5.72 hours, stirring speed of 1184.16 rpm, catalyst concentration of 2.35 mol, and a temperature of 64.18^{o}C. Under these conditions, the experimental yield was obtained to be 4.44% against the predicted yield of 4.07169%, hence with minimal error, the results of the statistical analysis showed that the process parameters (catalyst concentration, time, stirring speed and temperature) have significant effects on the response.

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