

# Multi-Response Optimization of Epoxidation Process Parameters of Rapeseed Oil Using Response Surface Methodology (RSM)-Based Desirability Analysis

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**Abstract** The primary efforts of this investigation stand focused on formulating a biodegradable lubricant with good thermo-oxidative stability and low pour point. Rapeseed oil was chosen to this end and was chemically modified via epoxidation, hydroxylation and transesterification processes. This study focuses on multi-response optimization of epoxidation of rapeseed oil with performic acid as oxygen carrier generated in situ. Experiments were conducted using full factorial central composite design. Response Surface methodology-based desirability analysis was employed for the optimization of process parameters namely reaction time and temperature based on the multiple performance characteristics including oxirane content and % conversion. The mathematical models were developed and tested for adequacy using analysis of variance, and other adequacy measures using the developed models. The main and interaction effects of the input variables on the predicted responses were also investigated. The optimization results showed that the reaction time of 3.23 h and the temperature of 70.74 °C were necessary to maximize oxirane content and % conversion in the epoxidation process.

**Keywords** Biodegradable lubricant · Central composite design · Epoxidation · Oxirane content · Response surface methodology

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## الخلاصة

تتركز الجهود الرئيسية لهذا التحقيق على صياغة مواد التشحيم القابلة للتحلل البيولوجي مع استقرار حراري مؤكسد جيد ونقطة صب منخفضة. وقد تم اختيار زيت بذور اللفت لهذه الغاية وتعديلها كيميائياً عبر عمليات الإيبوكسدة، إضافة إلى الهيدروكسيل والأسترة. وتتركز هذه الدراسة على التحسين متعدد الاستجابة لعملية الإيبوكسدة لزيت بذور اللفت مع حمض الفورميك وناقل الأكسجين المنتج داخلياً. وقد أجريت التجارب باستخدام تصميم مركب مضروب المركزي الكامل (CCD)، وطُبقت منهجية استجابة السطح (RSM) القائمة على تحليل الرغبة في تحسين معاملات العملية المسماة وقت ودرجة حرارة التفاعل المعتمدة على خصائص الأداء المتعددة بما في ذلك محتوى الإيبوكسايد ونسبة التحول، وطوّرت إلى جانب ذلك نماذج رياضية واختبر مدى تناسبها باستخدام تحليل التباين (ANOVA) وقياسات التناسب الأخرى باستخدام النماذج المتطورة. كما تم بحث التأثير الرئيسي والتفاعل بين متغيرات الإدخال في الاستجابات المتوقعة. وأظهرت نتائج التحسين أن وقت تفاعل بقيمة 3.23 ساعة ودرجة حرارة بقيمة 70.74 مئوية كانت ضرورية لتعظيم محتوى حلقة الإيبوكسايد ونسبة التحول في عملية الإيبوكسدة.

## 1 Introduction

Over the last few decades, lubricants were normally derived from petroleum feedstocks. In a situation marked by decline of petroleum, lubricants which depend upon petroleum for their production are prone to become scarce. The need for lubricant is increasing markedly owing to increasing vehicle movement. Vegetable oil, in particular rapeseed oil is an alternative raw material to produce automotive lubricant for the next generation. This factor assumes importance in the context of the world's too much reliance on petroleum-based oil. Consequently, non-renewable sources which are limitedly available can be saved as heritage for future generations. Furthermore, the availability of rapeseed oil as a raw material can be guaranteed since it is a renewable source. A high content of unsaturated bonds indicated by the high iodine value



of rapeseed oil allows higher yield, a key environment for economic production of rapeseed oil-based bio-lubricant [1].

Biodegradable lubricants were first developed for two stroke outboard engines in the early 1980s [2]. But vegetable oil in its natural form has limited use as industrial fluids due to poor thermal and oxidative stability. Many research groups have focused on adding commercially available antioxidants to the oil, preparing new antioxidants or genetically modifying plants from which vegetable oils are derived in an attempt to solve the problem [3]. Similarly, efforts have been made to improve the low temperature properties by blending vegetable oils with diluents such as poly  $\alpha$  olefin and diisodecyl adipate [4]. Attempts have been made to improve the oxidative stability and low temperature fluidity by transesterification of trimethylolpropane with *jatropha curcas* [5]. The unsaturated fatty acid molecule of the vegetable oil can be used to introduce various functional groups by being involved chemical modifications. Among them, epoxidation is one of the most widely used reactions. In the epoxidation step, unsaturated bonds in the rapeseed oil are converted to produce epoxy group indicated by the percentage of oxirane content. A high percentage of oxygen content in the epoxidized oil has more epoxy groups [6,7]. There are several methods for producing epoxides from vegetable oils. These include epoxidation with percarboxylic acid generated in situ in the presence of acids or enzymes as catalysts, epoxidation with organic and inorganic oxidants such as potassium peroxomonosulphate and meta-chloroperoxy benzoic acid [8,9]. Adhvaryu et al. [10] have demonstrated the improved performance of epoxidized soybean oil (ESBO) over bland soybean oil (SBO) and genetically modified high oleic soybean oil (HOSBO) for certain high-temperature lubricant application.

In the synthesis of biobased automotive lubricant, epoxidation reaction is a key aspect to obtain lubricant products with high oxirane content. Hence, the optimal operating condition in the epoxidation process must be clearly defined to achieve high content of epoxy groups. Further, a Taguchi method based on three levels and six variables L27 orthogonal array robust design was implemented to optimize the process parameters of enzymatic synthesis of xylitol fatty acid ester [11]. Similarly, response surface methodology (RSM) was used to study and optimize the effects of variables (reaction temperature, enzyme load, mole ratio of  $H_2O_2/C-C$  bonds, and reaction time) on the epoxy oxygen group content (EOC) of epoxidized *sapindus mukorossi* seed oil [12]. The epoxidation of rapeseed oil (RO) with peracetic acid generated in situ by the reaction of 30 wt% hydrogen peroxide and acetic acid has been studied and followed by optimization studies through statistical experimental design methodology with the utilization of a rotatable uniform design [13]. Desirability functions have been used extensively to simultaneously optimize several responses. Since the original formulation of these functions contains non-differentiable points,

only search methods can be used to optimize the overall desirability response [14].

Epoxidation reaction is a crucial step to produce a high quality of bio-lubricant as indicated by high oxirane content with reasonable viscosities. However, far too little attention has been paid to the utilization of rapeseed oil as a potential raw material to produce biodegradable low temperature automotive lubricant. Therefore, intensive research needs to be conducted to investigate the key process variable (reaction time and reaction temperature) in the epoxidation process that influence the final quality (oxirane content and % conversion) of the epoxidized products. In the present work, we report the optimized formulation of biodegradable lubricant from epoxidized rapeseed oil using response surface methodology (RSM)-based desirability approach.

## 2 Materials and Methods

The raw materials for this study of the epoxidation reaction were high grade rapeseed oil procured from a local oil dealer; 0.1 N thio solution, AR grade 30 wt% hydrogen peroxide, 90 wt% formic acid, 98 wt% concentrated Sulfuric acid and methanol, p-Toluene sulphonic acid used for hydroxylation reaction were procured from Loba Chemie, Mumbai, India. Table 1 shows the fatty acid composition of rapeseed oil.

### 2.1 Experimental Design

Response surface methodology is a collection of statistical and mathematical technique useful for developing, improving and optimizing processes. RSM is an important branch of experimental design and is a critical technology in developing new processes and optimizing their performance. The objectives of quality improvement, including reduction of variability and improved process and product performance, can often be accomplished directly using RSM [15–17]. In the present study, RSM was performed to determine the optimal operating condition in the epoxidation reaction by applying a second-order polynomial model with two independent variables namely, reaction time and temperature. A full fac-

**Table 1** Fatty acid composition of rapeseed oil

Fatty acids	Composition (wt %)	Lipid numbers
Palmitic acid (C <sub>16</sub> H <sub>32</sub> O <sub>2</sub> )	4	16:0
Stearic acid (C <sub>18</sub> H <sub>36</sub> O <sub>2</sub> )	1.5	18:0
Oleic acid (C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> )	17	18:1
Linoleic acid (C <sub>18</sub> H <sub>32</sub> O <sub>2</sub> )	13	18:2
Linolenic acid (C <sub>18</sub> H <sub>30</sub> O <sub>2</sub> )	9	18:3
Erucic acid (C <sub>22</sub> H <sub>42</sub> O <sub>2</sub> )	41	22:1
Palmitoleic acid (C <sub>16</sub> H <sub>30</sub> O <sub>2</sub> )	14.5	16:1



torial central composite design (CCD) was performed with a total number of treatment combination of

$$2^k + 2k + n_o$$

where  $2^k$  is the factorial design ( $2^2 = 4$ ),  $2k$  is the star point ( $2 \cdot 2 = 4$ ),  $n_o$  is the replication at the central points (3), and  $k$  is the number of independent variables (2).

The central values for epoxidation reaction for two independent variables happened to be 4 h of reaction time and of temperature 60 °C. The two independent variables to be optimized were coded as  $X_1$  and  $X_2$  at five levels (−2, −1, 0, 1 and 2) using the equation below:

$$X_i = (x_i - x_o) / \Delta x_i \quad (1)$$

where  $X_i$  is the coded value of the independent variable,  $x_i$  is the real value of independent variable,  $X_o$  is the real value of independent variables at center point, and  $\Delta x_i$  is the step change value (interval).

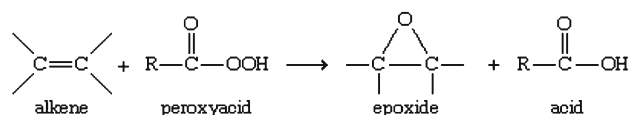
Hence, 11 experiments were conducted for the epoxidation of rapeseed oil using formic acid as an oxygen carrier and the results were fitted with second-order polynomial model. The range and level of the variables investigated are listed in Table 2 whereas the experimental design is illustrated in Table 3.

Design-Expert<sup>®</sup> 8.0 was used to code the variables and to establish the central composite design matrix and to establish

the design matrix to analyze the experimental data and to fit the experimental data to a second-order polynomial. The statistical significance of the terms in each regression equation was examined using the sequential  $F$  test, lack-of-fit test, and other adequacy measures using the same software to obtain the best fit. In order to optimize the process parameters, the numerical optimization technique was used. Using analysis of variance (ANOVA), the significance of input parameters was evaluated. Sequential  $F$  test, lack-of-fit test, and other adequacy measures were used to check the model's performance.

## 2.2 Epoxidation Process

The general process for synthesis of epoxide group is known as epoxidation reaction wherein an alkene is reacted with an organic peroxy acid. The simplified epoxidation reaction is summarized as follows.



The epoxidation of rapeseed oil is carried out in a batch type glass reactor consisting of a four necked round bottom flask of 500 ml capacity. A motor driven speed regulator stirrer was inserted in the reactor through the central neck while the other neck was used for inserting thermometer. A reflux condenser fitted to the reactor through the third neck and the fourth neck was used for dropping the raw materials into the reactor through the dropping funnel. The reactor was heated by an electric heating mantle having an arrangement for accurate control of the temperature within  $\pm 1$  °C of the desired temperature. A photographic view of the experimental setup for the epoxidation reaction is illustrated in Fig. 1a.

Prior to the epoxidation reaction, rapeseed oil was analyzed to determine its iodine value. Rapeseed oil of 326 ml, 0.3253 mol was placed in 500 ml four necked round bottom flask. Formic acid of 31.4 ml, 0.813 mol at a molar ratio of 0.75:1 to the oil and 0.358 ml, 1 wt% of sulfuric acid catalyst were added to the contents and were mixed by means of a stirrer and it was maintained at 0–10 °C with the help of an ice bath. Then, 30 wt% hydrogen peroxide of 265.72 ml, 2.603 mol was added drop wise to the reaction mixture at a rate such that the hydrogen peroxide addition was completed in 15 min. This feeding strategy was required to avoid the overheating, as the epoxidation reaction is highly exothermic. Further, the contents were well mixed and were performed at a stirring speed of 300 rpm. The temperature was then raised slowly to the required temperature by keeping four necked flask in hot water bath as shown in Fig. 1b and maintained at the same temperature using a magnetic stirrer. The product of the reaction was cooled and decanted to effect

**Table 2** Range and level of variables

Variables	Symbol coded	Range and level				
		−2	−1	0	1	2
Reaction time (h)	$X_1$	2	3	4	5	6
Temperature (°C)	$X_2$	40	50	60	70	80

**Table 3** Experimental design

Experiment no.	$X_1$	$X_2$	Experimental design
1	−1	−1	2 <sup>2</sup> Full factorial design (4 Experiments)
2	1	−1	
3	−1	1	
4	1	1	
5	−2	0	2*2 Star points (4 Experiments)
6	2	0	
7	0	−2	
8	0	2	Central points (3 Experiments)
9	0	0	
10	0	0	
11	0	0	

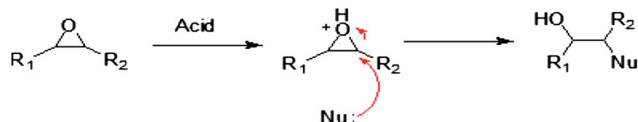


**Fig. 1** a, b Epoxidation process

a separation of the epoxidized oil from the water phase. The epoxidized oil was then washed with warm water in small aliquots to remove residual contaminants.

### 2.3 Ring Opening and Esterification Process

The term ring opening reaction is used to refer the process of introducing hydroxyl groups into unsaturated bonds to the oil. There are various sources of hydroxyl groups that can be used in the hydroxylation process such as alcohol and water. Before the hydroxylation reaction occurs, the oxirane ring must be opened. In the present work ring opening using an acid catalyst was performed. The mechanism of this process is described below:



The procedure for ring opening and the esterification reaction of the ring opened product was adapted from our previous study [18]. Finally, the yield was obtained by comparison of the amount of isolated product with the theoretical amount of oxirane content. Replication of each experiment was performed alongside to determine the percentage deviation between two experimental results and deviation was found to be <5 %.

### 2.4 Epoxidation Test

This analysis is used to evaluate the yield of the epoxidation reaction in terms of two key variables namely, iodine value and oxirane oxygen content. Iodine value was determined by applying Wijs method, i.e., 0.1–0.5 g of sample was placed into the flask and 10 ml of chloroform was then added to the sample. Following this, a 15 ml Wijs iodine

solution was added. Using the same procedure, blank solution was also prepared. The mixture was then stored in a dark place for at least 30 min at a temperature of  $25 \pm 5$  °C and after that, 10 ml, 15 wt% of potassium iodide (KI) solution and 50 ml of water were added to the mixture. The iodine content in the mixture was then titrated using 0.1 N sodium thiosulfate solution until the yellow color of the solution almost disappeared. A few drops of starch indicator solution were then added and titration was continued until the blue color completely disappeared. The iodine value and % conversion was calculated using the following equation:

$$\text{Iodine value (IV)} = [(B - A) \times N \times 12.69] / C$$

where  $A$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the sample (ml),  $B$  is the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the blank solution (ml),  $C$  is the weight of sample, g, and  $N$  is the normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

$$\% \text{Conversion} = \{(IV_0 - IV) / IV_0\} \times 100$$

where  $IV_0$  is the initial iodine value and  $IV$  is the iodine value at certain condition.

The oxirane content of the epoxidized oil must be quantified to determine the conversion of unsaturated bonds in rapeseed oil to oxirane group. A calculated amount of epoxidized oil was added into a flask. Ethyl ether of 5 ml was used to wash the flask inside and then 10 ml of the hydrochlorination reagent (0.2 N HCl in ethyl ether) was added into the flask. Simultaneously, a blank solution was prepared using an identical procedure. The mixture was then allowed to stand for 3 h at room temperature, and then titrated with standard 0.1 N sodium hydroxide solution. Prior to this, a few drops of phenolphthalein indicator solution and 50 ml of ethanol were added. The percentage of oxirane content was calcu-

**Table 4** Observed responses

Expt no.	Time	Temperature	Conversion (%)	Oxirane content (%)
1	3	60	51.44	5.8
2	3	40	11	4.84
3	2	50	30.31	4.84
4	4	50	51.46	5.35
5	1	60	36.45	4.95
6	3	60	48.51	5.81
7	5	60	64.14	5.59
8	2	70	51.58	5.67
9	4	70	67.55	5.51
10	3	80	76.32	5.39
11	3	60	48.93	5.77

lated using the following equation:

$$\% \text{oxirane content} = [(V_b - V_s) \times N \times 16 \times 100] / [W \times 1,000]$$

where  $V_b$  is the volume of NaOH used for blank, ml,  $V_s$  is the volume of NaOH used for sample, ml,  $N$  is the normality of NaOH, and  $W$  is the weight of the sample, g.

The observed responses are presented in Table 4.

### 3 Results and Discussion

#### 3.1 Fourier Transform Infrared (FTIR) Spectroscopic Analysis

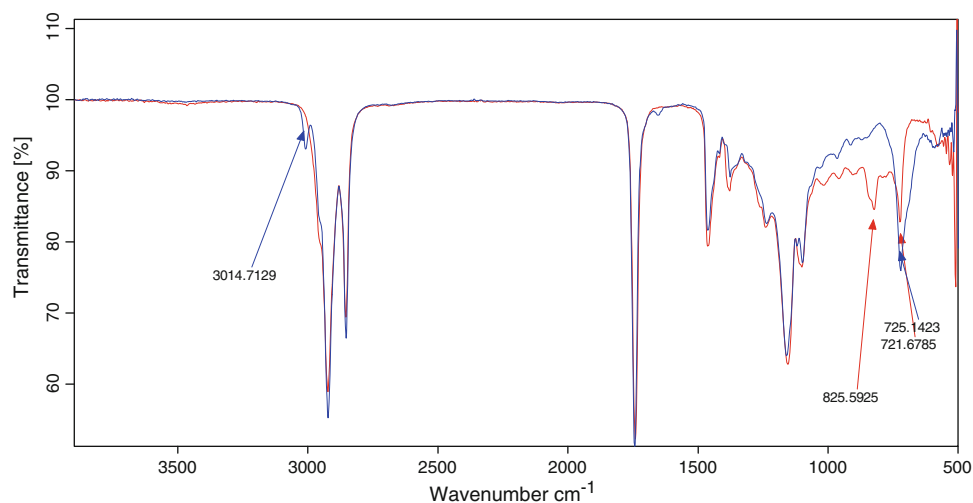
Bruker® Alpha T-FTIR spectrometer, Germany was used for monitoring the disappearance of double bonds and formation of epoxy groups during the reaction by qualitative identifica-

tion of main signals. Overlaid infrared transmittance spectra are shown in Fig. 2. Main IR peaks and their corresponding functional groups are listed in Table 5.

Following are the characteristics of the FTIR spectra of epoxidized oils, which confirm that the epoxidation has taken place. Disappearance of the band at  $3,014.71 \text{ cm}^{-1}$  shows C=C has been used up. The appearance of a band at  $825.59 \text{ cm}^{-1}$  which is not seen in raw oil is characteristic of the epoxide and it can be assigned to ring vibrations of the epoxy ring in cis-epoxides [19]. The presence of epoxy groups at  $822\text{--}833 \text{ cm}^{-1}$  also agrees with the study [20]. Furthermore, the epoxy ring opening reaction could occur either by acid catalysis in the presence of water associated with  $\text{H}_2\text{O}_2$  used. The hydrolysis of the ester group during epoxidation reaction in oil is the main side reaction. The band corresponding to the carboxylic acid group is located at  $1,650 \text{ cm}^{-1}$  and is usually very intense even at low carboxylic group concentrations. In case of hydrolysis, a carboxylic acid functional group is formed and this carbonyl group will appear near but differentiable of the ester carbonyl stretching C=O in the glyceride moiety at  $1,743.44 \text{ cm}^{-1}$ .

**Table 5** IR peaks and its functional groups

Frequency range ( $\text{cm}^{-1}$ )	Functional groups
2,850–2,860	C–H stretching of alkane
3,010–3,015	C–H stretching of non conjugated unsaturation
1,745–1,750	C=O stretching of esters
1,460–1,465	C–H bending of un saturated alkane
1,115–1,170	C–O stretching of esters
825–830	C–O stretching of epoxy oxirane oxygen
720–730	C–C bending of saturated C atom

**Fig. 2** Overlaid FTIR spectra of raw and formulated oil

C:\Program Files\OPUS_65\MEAS\rape seed oil-14-11.0	rape seed oil-14-11	Instrument type and / or accessory	14/11/2011
C:\Program Files\OPUS_65\MEAS\rape seed oil-epox-14-11.0	rape seed oil-epox-14-11	Instrument type and / or accessory	14/11/2011

**Table 6** Tested properties of raw and formulated oil

Properties	Standard [24–27]	Raw oil	Formulated oil
Oxirane content (%)	AOCS Cd 9-57	–	5.81
Rotary bomb time (min)	ASTM D2272	16	35
Biodegradability (%)	CEC-L-33-A93	>95	>95
Iodine value	AOCS Cd 1-25	120	5.1
Wear scar diameter (mm)	ASTM D4172	0.6	0.65
Viscosity index	ASTM D2270	220	160
Color	–	Brownish yellow	Pale yellow
Density @ 15 °C (kg m <sup>-3</sup> )	ASTM D1298	922	966.5
Flash point (°C)	ASTM D93	320	240
Pour point (°C)	ASTM D97	–11	–15
Viscosity @ 40 °C (mm <sup>2</sup> s <sup>-1</sup> )	ASTM D445	35	90.1
Viscosity @ 100 °C (mm <sup>2</sup> s <sup>-1</sup> )	ASTM D445	8	31

However, in the course of the epoxidation reaction carried out in our study, no evidence of the carbonyl from carboxylic acid group signal was observed. Further, the various tribological properties of the formulated oil were tested as per the ASTM standard. Table 6 shows some of the tested properties of raw and formulated oil.

### 3.2 Development of RSM-Based Models

In the present work, mathematical models were developed for the performances namely oxirane oxygen content and % conversion. RSM requires the experiments to be conducted as per the design of experiments [21]. A five-level second-order face central composite design was adapted to study linear, quadratic, and two-factor interaction effects. In the present study, two parameters namely reaction time and temperature were identified and the ranges of the parameters were selected based on the preliminary experiments. The variables at the intermediate (0) level constitute the center points and the combination of each of the variables at either its lowest (–2) or highest (+2) with the other two variables of the intermediate levels constituting the star points. The trials in the design matrix indicate the sequence run number and  $X_1$  and  $X_2$  represent the notation used for the variables, i.e., reaction time and temperature. In order to study the effect of the process parameters on the % conversion and oxirane content, a second-order polynomial response surface can be fitted into the following equation.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (2)$$

where  $Y$  is the response ( $Y_1 = \text{Oxirane content}$ ,  $Y_2 = \% \text{ conversion}$ );  $\beta_0$  is a constant;  $\beta_1$  and  $\beta_2$  represent the regression coefficient; while  $\beta_{11}$  and  $\beta_{22}$  are the quadratic coefficients; and  $\beta_{12}$  is the interaction coefficient. The second-order response surface  $Y$  can be expressed as a function of the process parameters, such as the time ( $X_1$ ) and temperature ( $X_2$ ) in Eq. (2).

The final mathematical models in coded factors/variable forms as determined to predict oxirane content and the % conversion are given below:

$$\begin{aligned} \text{Oxirane content} = & 5.84187 + 1.90208 X_1 + 0.26642 X_2 \\ & - 0.01675 X_1 X_2 - 0.12687 X_1^2 \\ & - 1.65625 X_2^2 \end{aligned}$$

$$\begin{aligned} \% \text{ Conversion} = & -81.55409 + 15.47833 X_1 + 1.78850 X_2 \\ & - 0.12950 X_1 X_2 \end{aligned}$$

### 3.3 Analysis of Developed Quadratic Model

The adequacy of the developed models was tested at 95 % confidence interval using ANOVA technique, and the results of the linear and quadratic order response surface model fitting in the form of ANOVA are given in Tables 7 and 8. The test for the significance of the regression models, the test for significance on individual model coefficients and the lack-of-fit test were performed using the same statistical Design-Expert 8.0 software package. By selecting the step-wise regression method, which eliminates the insignificant model terms automatically, Tables 7 and 8 also show the other adequacy measures  $R^2$ , adjusted  $R^2$ , and predicted  $R^2$ . The coefficient of determination  $R^2$  indicates the goodness of fit for the models, which provides a measure of variability in the observed response values and can be explained by the controllable factors and their interactions. In this case, all the values of the coefficient of determination  $R^2$  are nearly equal to 1. The adjusted coefficient of determination  $R^2$  is a variation of the ordinary  $R^2$  statistic that reflects the number of factors in the model. The entire adequacy measures are closer to 1, which is in reasonable agreement and indicate adequate models.

The adequate precision “Adeq Precision” compares the range of predicted value at the design points to the average prediction error. Adequate precision measures signal to noise ratio for which a ratio greater than 4 is desirable. In all cases, the value of adequate precision is dramatically greater than 4. The adequate precision ratio above 4 indicates the adequate model discrimination. Tables 7 and 8 also show the model terms standard deviation (SD), mean, coefficient of variation (CV), and PRESS. Standard deviation (SD) is a square root of the error mean square  $\sqrt{\text{MSE}}$  and “CV” is the coefficient of variation, defined  $(\frac{\sqrt{\text{MSE}}}{y})100$ , where  $y = \text{mean}$ . The CV measures the unexplained or the residual variability in the data as a percentage of the mean of the response variable. At

**Table 7** ANOVA for oxirane content

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Model	3,071.72893	3	1,023.91	32.94663	0.0002	Significant
X <sub>1</sub> -time	341.865376	1	341.8654	11.0003	0.0128	
X <sub>2</sub> -temperature	2,352	1	2,352	75.68098	<0.0001	
X <sub>1</sub> X <sub>2</sub>	6.7081	1	6.7081	0.215848	0.6563	
Residual	217.544758	7	31.07782			
Lack of fit	212.524291	5	42.50486	16.93263	0.0567	Not significant
Pure error	5.02046667	2	2.510233			
Cor total	3,289.27369	10				
R <sup>2</sup>	0.933					
Adj R <sup>2</sup>	0.905					
Predicted R <sup>2</sup>	0.8					
Adeq precision	16.65					
CV	11.4					
PRESS	759					
Mean	48.87					
SD	5.57					

**Table 8** ANOVA for the % conversion

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	
Model	1.31278258	5	0.262557	12.5856	0.0074	Significant
X <sub>1</sub> -time	0.01860119	1	0.018601	0.891645	0.3884	
X <sub>2</sub> -temperature	0.00053987	1	0.00054	0.025879	0.8785	
X <sub>1</sub> X <sub>2</sub>	0.112225	1	0.112225	5.379484	0.0681	
X <sub>1</sub> <sup>2</sup>	0.31070278	1	0.310703	14.89348	0.0119	
X <sub>2</sub> <sup>2</sup>	0.52947421	1	0.529474	25.38024	0.0040	
Residual	0.10430833	5	0.020862			
Lack of fit	0.10344167	3	0.034481	79.57051	0.0124	Not significant
Pure error	0.00086667	2	0.000433			
Cor total	1.41709091	10				
R <sup>2</sup>	0.926					
Adj R <sup>2</sup>	0.852					
Predicted R <sup>2</sup>	0.815					
Adeq precision	9.476					
CV	2.67					
PRESS	0.88					
Mean	5.41					
SD	0.14					

the same time, relatively lower values of the CV from Tables 7 and 8 indicate improved precision and reliability of the conducted experiments. “Prediction error sum of squares” (PRESS) is a measure of how well the model for the experiment is likely to predict the responses in a new experiment. Smaller values of PRESS are desirable. In all the cases, the values of PRESS are considerably smaller. The values of “Probability > F” in Tables 7 and 8 for all models are <0.05 and these indicate that all models are significant. In all cases,

the “Lack-of-fit” value implies that the “Lack-of-fit” is not significant relative to the pure error. Nonsignificant lack of faith as it is desired is good.

### 3.4 Optimization of the Epoxidation Process Parameters Through Numerical Optimization

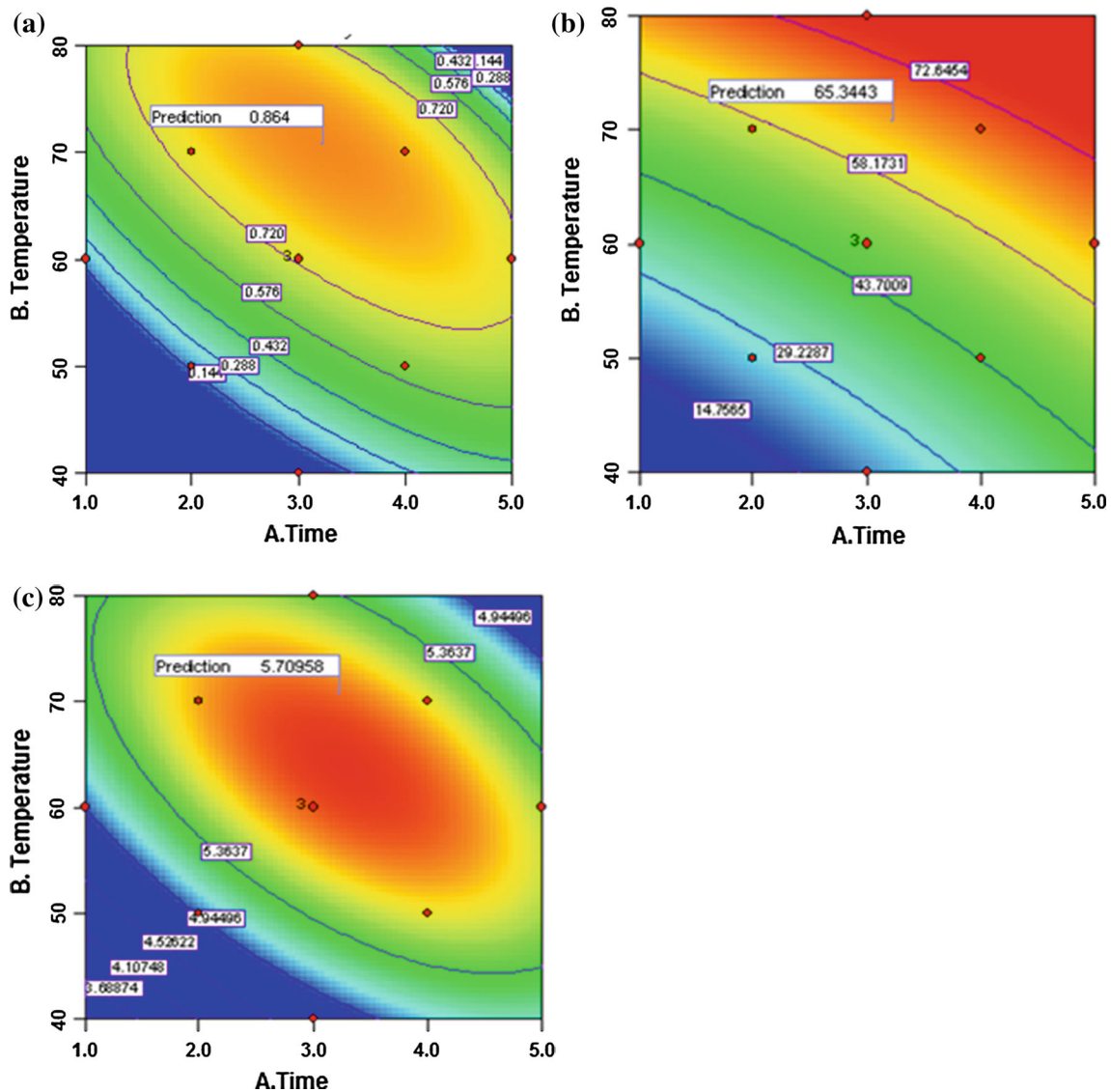
Optimization of process parameters assumes importance in the context of increase in productivity. The desirability-based

**Table 9** Goals set and limits used for the optimization

Parameter and response	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Reaction time	Is in range	1	5	1	1	3
Temperature	Is in range	40	80	1	1	3
Oxirane content	Maximize	4.84	5.81	1	1	3
Conversion (%)	Maximize	11	76.32	1	1	3

**Table 10** Best global solution for optimization

S. no.	Reaction time (h)	Temperature (°C)	Oxirane content	Conversion (%)	Desirability
1	3.23	70.7	5.71	65.34	0.864
2	3.2	70.2	5.51	64.23	0.860
3	3.1	70.2	5.41	64.13	0.859

**Fig. 3** Estimated contour plots **a** Desirability. **b** % Conversion. **c** Oxirane content



optimization technique has produced a unique and powerful optimization procedure that differs from traditional practices. In recent years, the desirability function approach is used by some of the researchers for finding the optimal solutions using multi-performance objective [21]. Desirability is an objective function that ranges from zero outside of the limit to one at the goal. The numerical optimization finds a point that maximizes the desirability function. The characteristics of a goal may be altered by adjusting the weight. All goals get combined into one desirability function for several responses and factors. It reflects the desirable ranges for each response ( $d_i$ ). The desirable ranges from zero to one (least to most desirable, respectively). The simultaneous objective function is a geometric mean of all transformed responses:

$$D = (d_1 \times d_2 \times \dots \times d_n)^{1/n} = \left( \prod_{i=1}^n d_i \right)^{\frac{1}{n}} \quad (3)$$

where  $n$  is the number of responses in the measure. If any of the responses or factors falls outside their desirability range, the overall function becomes zero.

The reaction time and temperature are the major epoxidation process parameters that were paid attention to these experiments. For maximizing oxirane content and the % conversion, optimization of process parameters are required. In this work, the multiple performance optimization of epoxidation parameters was carried out using response surface methodology-based on the desirability function approach. The goal set, the used lower limits, upper limits and weights, and the importance of the factors given are presented in Table 9. Different best solutions were obtained in desirability-based approach. But, as is would not in any pursuit, solution with high desirability is preferred. The best three solutions obtained for the optimization are presented in Table 10.

The optimization is carried out for combination of goals. The goals used for oxirane content and the % conversion are “maximize” and the goals used for the factors are “within range”. A weight can be assigned to a goal to adjust the shape of its particular desirability function. The solutions are sorted with the most desirable preferred first. By default, the input factors are set range, thus preventing extrapolation. Estimated contour plots for desirability, oxirane content and the % conversion are presented in Fig. 3a–c. These response contours can help in the prediction of desirability at any zone of the experimental domain [14]. From the figure, it is depicted that the increase in temperature and reaction time increases the desirability and vice versa. The optimization results showed that reaction time at 3.23 h and temperature at 70.74 °C are necessary to maximize the oxirane content and the % conversion in the epoxidation process.

The variation of % oxirane oxygen content with the reaction time and temperature is presented as a 3D response graph is shown in Fig. 4. From the figure, it could be seen

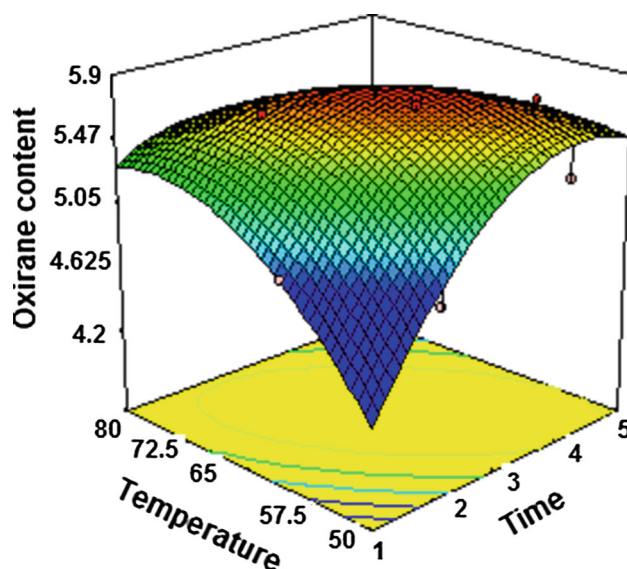


Fig. 4 Estimated 3D surface plot for oxirane content

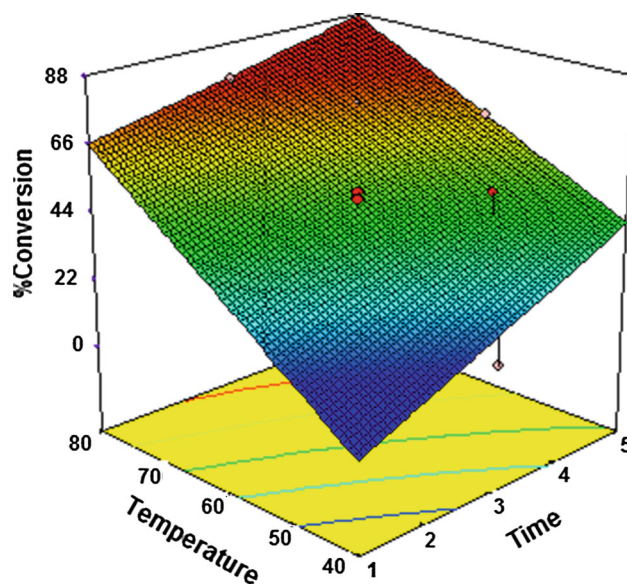


Fig. 5 Estimated 3D surface plots for reaction conversion

that the value of oxirane content increases with reaction time and temperature and then that value reaches the maximum level. Following this, the oxirane content decreases with reaction time and temperature. The maximum oxirane content of 5.67 % was achieved at a reaction time 3.23 h and at a reaction temperature 70.74 °C. Another important finding was that at higher reaction time and temperatures than the optimal condition, a lower oxirane content will result. This is a result of a high temperature of the epoxidation reaction favoring a high rate of oxirane ring opening thereby producing a product with reduced oxirane content. Similarly, higher side reaction products are formed above the optimal temperature such as reaction between oxirane ring and water and eventually

**Table 11** Plan of confirmation experiments and results

Trial no.	Reaction time (h)	Temperature (°C)	Oxirane content		Conversion (%)	
			Predicted	Experimental	Predicted	Experimental
1	3.23	70.7	5.67	5.78	65.34	64.95
2	3.23	70.7	5.67	5.81	65.34	65.20

a dimerization reaction may occur. Furthermore, epoxidation reaction using peroxyformic acid is highly exothermic. Hence, high temperature during the epoxidation reaction may cause higher rate decomposition of epoxy groups than the formation rate. As a result, lower epoxy groups will be produced. At a higher temperature, the relative conversion to oxirane increased to an optimal point and then declined gradually in the epoxidation of cottonseed oil. These findings are also consistent with the previous study [22].

The variation of the reaction conversion values with the reaction time and temperature is presented as a 3D response graph as shown in Fig. 5. The result indicates that the conversion of iodine value in the rapeseed oil increases linearly with the increase of reaction time and temperature, and at a faster rate with temperature than with reaction time. Unsaturated double bonds present in the oil converted into oxirane rings through the epoxidation reaction as indicated by the decrease in iodine value. This value in rapeseed oil represents the concentration of double bonds which decreases with reaction time. Therefore, the reaction conversion increases with reaction time and temperature. The findings also support previous research with the utilization of cottonseed oil as a raw material to produce epoxidized oil [22]. This result can be explained by the fact that through epoxidation reaction, double bonds in the oil were converted to epoxidized oil. A model that can illustrate the rate constant, which increases with temperature is described in Arrhenius law [23].

$$k = k_0 e^{-E/RT}$$

where  $k_0$  is the frequency factor,  $E$  is the activation energy,  $R$  is the gas constant, and  $T$  is the absolute temperature in K.

From the above equation, it is clear that reaction constant ( $k$ ) is a function of reaction temperature ( $T$ ). If the reaction temperature goes up, the reaction constant value will increase. Hence, it will increase the reaction rate of epoxidation and in this case a higher final conversion had resulted.

### 3.5 Confirmation Experiments

In addition to statistical validation, the developed models have also been validated by the confirmation experiments. Details of confirmation experiments are given in Table 11. Each of the confirmation experiments was repeated twice and the average values were tabulated. The predicted values are very close to the experimental results and hence, the devel-

oped model is suitable for predicting the responses in process parameters of the epoxidation process.

## 4 Conclusions

The formulation of rapeseed oil-based bio-lubricant through a chemical modification processes such as epoxidation, hydroxylation and esterification was clearly demonstrated and the formation of epoxy and hydroxyl group was confirmed by Fourier Transform Infra Red (FTIR) spectroscopy analysis. The epoxy signals were well identified and intensity of the signals due to the double bond vibration was evidenced by the spectroscopic techniques used. The result of the present investigation shows that rapeseed oil can be successfully utilized for epoxidation using peroxy acid generated in situ. The optimized parameters to get higher degree of epoxidation to minimum epoxy ring breaking were noted as reaction temperature of 70.74 °C and reaction time of 3.23 h. Under these optimum conditions, 5.67 % oxirane oxygen content in synthesized rapeseed oil was obtained. The synthesized epoxidized rapeseed oil is an attractive intermediate for the formulation of biodegradable lubricant. Further research efforts are necessary for the optimized formulation of bio-lubricant by considering more variables and levels, and their accuracy can also be improved by carrying out of Chi-squared fit test.

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