Research Article

Optimization of Partial Epoxidation on *Jatropha curcas* Oil Based Methyl Linoleate Using Urea-hydrogen Peroxide and Methyltrioxorhenium Catalyst

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Abstract

Natural epoxy fatty acids such as Coronaric acid (9,10-epoxy-12Z-octadecenoic acid) and vernolic acid (12,13-epoxy-9Z-octadecenoic acid) are rich in of *Vernolia galamensis*, *Vernolia anthelmintica* and *Chrysanthemums coronanium*. The two fatty acids each contains an oxirana ring and a double bond C = C. The oil or its derivatives are suitable for industrial usage as reactive diffluent of alkyd resins, plasticizers and stabilizers, surface coatings, surfactants and lubricants, as intermediates in chemical reactions for making linear epoxides of composite materials and polymers. However, the use of such oils on an industrial scale is impossible due to limited resources. Therefore, epoxidation reactions need to be carried out to overcome the demand for partial epoxide fatty acids. Partially epoxidation of methyl linoleate at room temperature (30°C) in the presence of pyridine, methyltrioxorhenium (MTO) as catalyst and urea-hydrogen peroxide (UHP) as oxidant was studied by using response surface methodology (RSM). A five-level-four-factors central composite rotatable design (CCRD) was used to optimize the partially epoxidation conditions and study the effect of MTO, UHP, pyridine and reaction time on relative conversion to oxirane (RCO). Quadratic polynomial model was employed to generate response surface plots for RCO. At optimal condition, 79.05% monoepoxide was formed at the RCO of 58.15% under condition of 0.75 mol% mole ratio of MTO, 300 mol% mole ratio of UHP and 9 mol% of pyridine at 120 min reaction time. It can be concluded that the effect of UHP mole ratios was the dominant factor to control the degree of partial epoxidation of methyl linoleate followed by mole ratio of MTO, reaction time and mole ratio of pyridine to formed methyl 12,13-epoxy-9Z-octadecenoate or/and methyl 9,10-epoxy-12Z-octadecenoate.

Keywords: Partially epoxidation, Methyltrioxorhenium, Urea-hydrogen peroxide, Response surface methodology (RSM), Central composite rotatable design (CCRD)

1 Introduction

Modified plant oils and their derivatives in chemicals industry are drawing numerous attractions in various applications due to their availability from renewable resources, biodegradable and non-toxic nature. Variety of chemical and biochemical reactions have been used for their conversion into value-added products. Among these, epoxidation reaction plays an important role in developing new chemicals. Epoxidation is the useful chemical reaction in which a double bond C = C of olefins is converted to an oxirane ring following reaction as below (Scheme 1).

The triangular-shaped oxirane ring is easily reacted and switched to another functional group due to its reactive and unstable ring. Therefore epoxidation is one of the useful modification reactions of a molecule. Removal of olefin groups in epoxidation reactions

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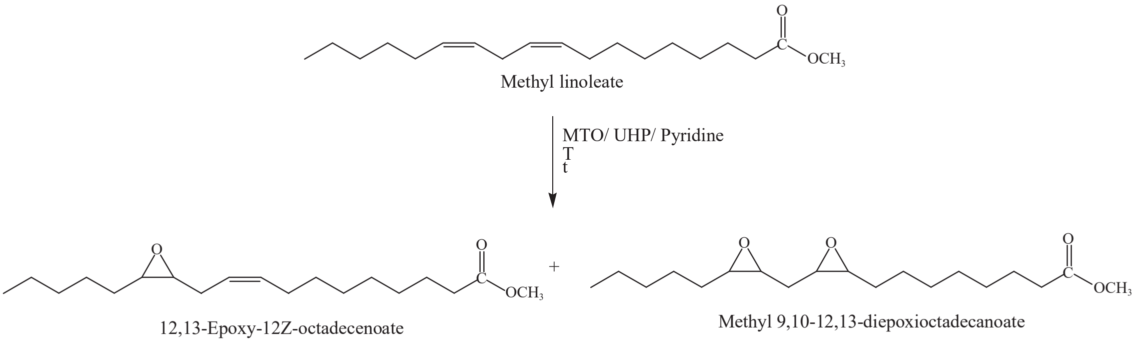


Scheme 1: Chemical reaction for the epoxidation of methyl linoleate.

improves the physicochemical properties of plant oils or their derivatives. Epoxidised plant oils have high viscosity, high oxidation stability, low tendency to form sediments and boundary lubricating properties similar to native plant oils. For example, epoxidised soybean oil shows maximum improvement in oxidation stability compared to genetically modify high-grade soybean oil and regular soybean oil. Epoxidation reactions can be partially or completely performed. When the degree of epoxidation is controlled, the nature of the resulting product can also be controlled. Oil or derivatives of complete or partial epoxidised oils have different physicochemical properties and are used in different domains. The epoxidised products have many useses in different markets, such as epoxidised soy oils as polyvinyl chloride plasticizers and stabilizers due to their ability to catch free hydrogen chloride to slow down degradation process [1], surface coatings, surfactants and lubricants, acid scavengers, as intermediates in chemical reactions [2]–[4] for making linear epoxides for derivatisation for composite materials and polymers, hydroxy compounds, glycol, alkanolamine, carbonyl compounds, making 1,2-diols for personal care or complicated ring epoxides for fragrance and flavouring as well as intermediates for pharmaceutical and agrochemicals. Partially epoxidised oil also drawing attentions in reactive diffluent for alkyd resins which include paints and surface coating materials. The homogenous with low viscosities and melting points below room temperature of partially epoxidised oils, acids, or their esters are desirable feature for reactive diffluent [5], [6].

The most preferred method of epoxidation of olefin compounds is epoxidation with organic (formic and acetic) and inorganic acids (sulfuric, hydrochloric and phosphoric) or enzyme (lipase, peroxigenase) catalyst. Epoxidation with peroxide acid catalytic is known as Prilezhaev epoxidation. However acid and enzymatic catalyst always drives side reaction of oxirane ring opening. On the other hand the use of various transitional metal catalysts in epoxidation has shown an excellent in regioselection or enantioselection properties. Methyltrioxorhenium (MTO) has been known as an effective transition metal-based catalyst for epoxidation of olefins [7]. Owing to the adjustable degree of epoxidation by using MTO-catalysed system, partially epoxide can be performed easily [6]. Hydrogen peroxide acted as an oxidant in most of the MTO-catalysed epoxidation. For instance, monoepoxides of methyl linoleate (the intermediate) for synthesizing linoleic acid diol glucuronides were formed by MTO with hydrogen peroxide system [8]. However, the MTO with hydrogen peroxide as oxidant (MTO/H_2O_2) system retarded the formation of epoxide with high yield. These limitation included the ring opening of newly formed epoxide due to the acidic nature of the rhenium catalyst and the facile decomposition of MTO to perrhenates [9]. Several improvements of the original procedure have been published to overcome this problems. The usage of urea-hydrogen peroxide (UHP) rather than hydrogen peroxide as an oxidant in order to avoid unwanted epoxide ring opening reactions in non-polar aprotic solvent [10]. The urea which was remained during the consumption of UHP modulate the pH of the solution and prevented the acid-catalysed ring opening process [11]. Furthermore, the addition of heterocyclic amine additives, such as pyridine, 3-cyanopyridine and pyrazole has been found to be successful in both suppressing such side reactions and substantially increasing the rate of epoxidation [9], [12], [13].

Traditionally, optimization study of epoxidation is performed by monitoring the influence of one factor at a time on an experimental response while keeping the other factors constant. This is called one-variable-at-a-time technique. However, this technique is time-consuming and does not include interactive effects among the variables and response [14]. Therefore, response surface methodology (RSM) was proposed in this study. It was not only a statistical and mathematical technique for locating the optimum conditions but also analysing how sensitive the optimum conditions varied between the multi variables. Herein, the advantage of the RSM was minimizing the experiment numbers meanwhile reduced the production cost, time and wastage [15]. RSM has been used for example for the esterification of acetic acid with methanol in a process simulation [16], to study the effect of organic acid pretreatment on napier grass (*Pennisetum purpureum*) straw biomass conversion [17], alkyl imidazolium chloride pretreatment on rice straw biomass conversion [18] etc. with higher efficiency and high yeilds. There were abundant literatures on the use of RSM for processes development and optimization but few for epoxidation [19]–[21]. RSM had successfully been applied 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 epoxy oxygen group content of epoxidised Sapindus mukorossi seed oil [22].

In this study, partially epoxidation reaction was carried out at room temperature (30°C) in the presence of MTO as catalyst, UHP as an oxidant and pyridine as side reactions suppressant. The purpose of this study was to optimise the partial epoxidation of methyl linoleate reaction conditions to attain the highest composition of monoepoxide. The effects of individual factors (MTO to double bonds ratio, UHP to double bonds ratio, pyridine to double bonds ratio and reaction time) and their interactive effect on relative conversion to oxirane (RCO) by using RSM were also investigated.

2 Materials and Methods

2.1 *Materials*

Methyl linoleate with 2.7% methyl oleate by urea complexation method (iodine value = 175.14 g I_2/100g) was prepared from *Jatropha curcas* oil [15]. MTO and UHP were obtained from Aldrich. Pyridine and dichloromethane (CH_2Cl_2) were obtained from Systerm. Chemicals obtained were used as received. Fatty acid composition of *Jatropha curcas* oil used in the study is shown in Table 1.

Table 1: Fatty acid composition of *Jatropha curcas* Linn oil

Fatty Acid	Composition (%)
Palmitic, $C_{16:0}$	13.3 ± 0.1
Palmitoleic, $C_{16:1}$	0.5 ± 0.2
Stearic, $C_{18:0}$	6.7 ± 0.3
Oleic, $C_{18:1}$	41.5 ± 0.6
Linoleic, $C_{18:}$	38.0 ± 0.9

2.2 *Partial epoxidation of methyl linoleate using MTO/UHP/pyridine*

Partial epoxidation of methyl linoleate was carried out according to the method reported [8] with slight modification. About 0.25–1.25 mol% of MTO (per mole of double bonds of the ML percentage) was added to a suspension of UHP (100–300 mol%) in CH_2Cl_2 (5 mL) followed by the addition of pyridine (3–15 mol%). The amounts of MTO, UHP and pyridine were calculated according to the double bonds content in the methyl linoleate. The mixture was vigorously stirred (1100 rpm) for 10 min at room temperature (30°C) until the solution turned to yellow and remained unchanged throughout the reaction. A solution of methyl linoleate (3 g, 20.7 mmol of double bonds) in 10 mL of CH_2Cl_2 was added to the mixture and stirred at room temperature (30°C) for a specific time. After reaction completion, the reaction mixture was diluted with CH_2Cl_2 and washed with H_2O. Excess hydrogen peroxide from UHP in the yellow organic phase was decomposed by the addition of small amount of manganese dioxide (MnO_2) until the yellow colour totally disappeared. The organic phase was separated and washed with a saturated solution of sodium chloride. It was dried over anhydrous sodium sulphate and the solvent was removed by evaporation under vacuum.

2.3 *Analytical techniques*

Oxirane oxygen content (OOC): The evolution of the epoxidation reaction was monitored by measuring the OOC in accordance with the official and recommended practice of AOCS Cd 9-57 [23]. Under the prescribed conditions of this method, the oxygen was titrated directly with hydrogen bromide in acetic acid. From the OOC measurement, the relative conversion to oxirane (RCO) value was calculated from the following formula:

$$\text{Relative conversion to oxirane (RCO)} = \frac{\mathrm{OOC_{ex}}}{\mathrm{OOC_{th}}} \times 100$$

Where $\mathrm{OOC_{ex}}$ was the experimentally determined content of oxirane oxygen in 100 g of sample and $\mathrm{OOC_{th}}$ was the theoretical maximum oxirane oxygen in 100 g of sample. The $\mathrm{OOC_{th}}$ value was determined from the following equation [24]:

$$\mathrm{OOC_{th}} = \left\{ \frac{(\mathrm{IV_o}/2\mathrm{A_j})}{[100 + (\mathrm{IV_o}/2\mathrm{A_j})\mathrm{A_o}]} \right\} \times \mathrm{A_o} \times 100$$

Where $\mathrm{IV_o}$ was the initial iodine value of methyl linoleate (175.14 g $\mathrm{I_2}$/100g), $\mathrm{A_i}$ (126.9) and $\mathrm{A_o}$ (16.0) were the atomic mass of iodine and oxygen respectively.

2.4 *Instrument*

A gas chromatography with flame ionization detector (Shimadzu, 17A series) equipped with column BPX 70 (30 m × 0.25 mm × 0.25 µm film thickness; SGE) was used to determine composition of the monoepoxide. The conditions of GC analysis were as follows: split injection with split ratio 29 : 1; flow rate 0.3 mL/min; FID temperature 280°C; injector temperature 250°C; initial oven temperature 120°C and final oven temperature 245°C. The methyl monoepoxidised linoleate existent was confirmed by the aids of using GC Mass Spectrometer.

2.5 *Experimental design*

The optimization and effect of the multivariable on the response in the region of investigation was explored using response surface methodology (RSM) provided by Design-Expert software version 7.1.5 (Stat-Ease Inc., Minneapolis, USA). Central composite rotatable design (CCRD) was employed to study the responses in this work. It was widely used for fitting a second-order response surface. An initial screening step was carried out to select the major independent variable.

The four important independent variables in this study were amount of catalyst (MTO), oxidant (UHP), suppressant of side reaction (pyridine) and reaction time used in the partial epoxidation reaction. An increase in RCO is expected to occur at high mole ratios of MTO and UHP compared to low mole ratios. This increase in RCO value is due to the intermediate formation of monoperoxorenium and peroxorenium increases as the mole ratio of MTO and UHP increases. Thus, there are more double bonds C = C being attacked by oxygen to form the oxygen transfer complex and in turn enhance the epoxidation reaction. In contrast, the RCO value decreases at low mole ratios of MTO and UHP due to the lack of oxygen transfer complexes. Furthermore the addition of heterocyclic amine additives (pyridine) is found to be successful in both suppressing such side reactions and substantially increasing the rate of epoxidation.

Herein, mole ratio of MTO to C = C bonds (0.25–1.25 mol%), mole ratio of UHP to C = C bonds (100–300 mol%), mole ratio of pyridine to C = C bonds (3–15 mol%) and reaction time (60–180 min) were selected as independent variables. On the other hand, the response chosen was relative conversion to oxirane (RCO) in percentage. Each variable was coded at five levels is shown in the Table 2. The design is rotatable because the variance function (–2, –1, +1, +2) is constant for all setting experiment variables at the same distance from the centre point, 0 [25]. This five-level-four factors experimental design requires 30 experiments which consist of 16 factorial points and 8 axial points plus 6 replicate centre points (Table 3). All experiments were run in the randomized order to minimize errors in the experiments.

Table 2: Variables and experimental domain in the MTO-catalysed partially epoxidation study

Independent Variable	**Unit**	**Coded Variable**	**Coded Levels**				
			–2	**–1**	**0**	**1**	**2**
Catalyst (MTO) to double bonds ratio	mol%	A	0.25	0.50	0.75	1.00	1.25
Urea hydrogen peroxide (UHP) to double bonds ratio	mol%	B	100	150	200	250	300
Pyridine to double bonds ratio	mol%	C	3	6	9	12	15
Reaction time	min	D	60	90	120	150	180

Table 3: Central composite rotatable design arrangement and response for MTO-catalytic partially epoxidation on methyl linoleate

Type	A: MTO/C=C (mol%)	B: UHP/C=C (mol%)	C: Pyridine/C=C (mol%)	D: Reaction time (min)	OOC (%)	RCO (%)
Fact	0.50	150	6	90	2.90	29.18
Fact	1.00	150	6	90	3.98	40.04
Fact	0.50	250	6	90	4.16	41.85
Fact	1.00	250	6	90	5.53	55.63
Fact	0.50	150	12	90	3.26	32.80
Fact	1.00	150	12	90	4.19	42.15
Fact	0.50	250	12	90	4.14	41.65
Fact	1.00	250	12	90	5.68	57.14
Fact	0.50	150	6	150	3.32	33.40
Fact	1.00	150	6	150	4.46	44.87
Fact	0.50	250	6	150	4.76	47.89
Fact	1.00	250	6	150	6.38	64.18
Fact	0.50	150	12	150	3.64	36.62
Fact	1.00	150	12	150	5.00	50.30
Fact	0.50	250	12	150	4.98	50.10
Fact	1.00	250	12	150	6.83	68.71
Axial	0.25	200	9	120	2.98	29.98
Axial	1.25	200	9	120	5.89	59.26
Axial	0.75	100	9	120	2.95	29.68
Axial	0.75	300	9	120	5.78	58.15
Axial	0.75	200	3	120	4.32	43.46
Axial	0.75	200	15	120	4.67	46.98
Axial	0.75	200	9	60	3.67	36.92
Axial	0.75	200	9	180	5.34	53.72
Center	0.75	200	9	120	4.67	46.98
Center	0.75	200	9	120	4.63	46.58
Center	0.75	200	9	120	4.75	47.79
Center	0.75	200	9	120	4.94	49.70
Center	0.75	200	9	120	4.86	48.89
Center	0.75	200	9	120	4.81	48.39

2.6 *Statistical analysis*

A second-order polynomial was used to fit the experimental data and predict the individual variables. The model proposed for the response, Y was given below:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 \sum \sum_{i<j=2}^{4} \beta_{ij} x_i x_j + \varepsilon$$

Where Y was the predicted response for percentage of RCO; β_0, β_i, β_{ii} and β_{ij} were representing intercept, linear, quadratic and interaction regression coefficients respectively; x_i and x_j were coded independent variables or factors; ε was random error. The estimation of the interaction terms were only contributed by the factorial points while the axial points played the role in estimation of quadratic terms. In the part of centre runs, provided an internal estimate of error (pure error) and contributed toward the estimation of quadratic terms too [25], [26]. Moreover, the error was assumed to be independent with mean equal to zero, constant variance or scatter over all values of the independent variables and normally distributed. Data was processed using analysis of variances (ANOVA). The significant of regression equation was checked by the Fisher distribution (F-test). The accuracy and the ability of the model was evaluated by coefficient of determination (R^2) and the adjusted R^2. On the other hand, for verification of model adequacy, diagnostic tests were carried out such as residual analysis and lack-of-fit test. The fitted polynomial equation for percentage of RCO was expressed in the form of contour and surface plots in order to reveal the relationship between response and the multivariable.

3 Results and Discussion

3.1 *Development of regression model*

Before embarking on the verification of the model adequacy, various model (linear, two factor interaction, quadratic and cubic) was fitting to the experimental data for selection of an appropriate response surface model for the response. In this catalytic partial epoxidation study, the quadratic polynomial model was selected for RCO response surface model by Design-Expert software due to its highest order polynomial with significant additional terms and the model was not aliased. The quadratic polynomial equation in term of coded variables was given below:

$$\begin{aligned} RCO = {} & 48.06 + 7.00A + 7.28B + 1.23C + 3.72D + \\ & 1.18AB + 0.30AC + 0.66AD - 0.40BC + \\ & 0.85BD + 0.52CD - 0.65A^2 - 0.82B^2 - \\ & 0.50C^2 - 0.47D^2 \end{aligned}$$

The symbols of A, B, C, D represented to mole ratio of MTO to C=C bonds, mole ratio of UHP to C=C bonds, mole ratio of pyridine to C=C bonds and reaction time respectively.

3.2 *ANOVA and model fitting*

ANOVA is a statistical technique which used to determine the significance of the selected model and linear, quadratic as well as interaction effects of independent variables on the responses [19]. Furthermore, *p*-value is a tool for checking the significance of each terms in the model and the lower the *p*-value, the more significance of the corresponding coefficient is [25]. In general, the *p*-value less than 0.05 indicates that the model terms are significant while *p*-value greater than 0.05 indicates not significant. Table 4 shows the ANOVA results for RCO response surface from quadratic polynomial model. The *F*-value of the regression model for RCO response was 128.92 and *p*-value < 0.0001 indicated that the model terms were significant. From the ANOVA results, the linear effect of variables A, B, C and D as well as interaction and quadratic terms AB, BD, A^2 and B^2 (*p*-value < 0.05) contributed significantly to the model.

Table 4: Analysis of variance (ANOVA) for RCO response surface quadratic model

Source	Sum of Squares	DF[a]	Mean Square	*F*-value	Prob > F (*p*-value)
Model	2897.40	14	206.96	128.92	< 0.0001[b]
A	1177.26	1	1177.26	733.37	< 0.0001[b]
B	1272.11	1	1272.11	792.45	< 0.0001[b]
C	36.19	1	36.19	22.54	0.0003[b]
D	331.75	1	331.75	206.66	< 0.0001[b]
AB	22.11	1	22.11	13.78	0.0021[b]
AC	1.40	1	1.40	0.87	0.3654[c]
AD	6.98	1	6.98	4.35	0.0545[c]
BC	2.50	1	2.50	1.56	0.2308[c]
BD	11.54	1	11.54	7.19	0.0171[b]
CD	4.36	1	4.36	2.71	0.1202[c]
A^2	11.53	1	11.53	7.18	0.0171[b]
B^2	18.65	1	18.65	11.61	0.0039[b]
C^2	6.81	1	6.81	4.24	0.0572[c]
D^2	6.14	1	6.14	3.83	0.0693[c]
Residual	24.08	15	1.61		
Lack of Fit	17.16	10	1.72	1.24	0.4294[c]
Pure Error	6.92	5	1.38		
Total	2921.47	29			
Std. dev.	1.27		R^2	0.9918	
Mean	46.10		Adj R^2	0.9841	
C.V. %	2.75		Pred R^2	0.9628	
PRESS[d]	108.81				

[a] Degree of freedom.

[b] Significant at “Prob > F (*p*-value)” less than 0.05.

[c] Not significant at “Prob > F (*p*-value)” more than 0.05.

[d] Prediction error sum of squares

From the experimental design, there were replicated observations on the response at the same settings of the independent variables which required by the lack-of-fit test. Hence, the residual sum of squares can be partitioned into lack of fit and pure error components. The lack-of-fit test in Table 4 is testing the lack of fit for the RCO response on quadratic polynomial model. Large *p*-value (0.4294) implied that the lack-of-fit test was not significant relative to the pure error and the selected model was fitted. Therefore, the corrected quadratic polynomial equation in term of coded variables for partial epoxidation of methyl linoleate are as below:

$$\text{RCO} = 48.06 + 7.00\text{A} + 7.28\text{B} + 1.23\text{C} + 3.72\text{D} + 1.18\text{AB} + 0.85\text{BD} - 0.65\text{A}^2 - 0.82\text{B}^2 - 0.50\text{C}^2 - 0.47\text{D}^2$$

In terms of model precision, high degree of precision for the experimental data was expressed by low values of standard deviation (Std. dev.) 1.27 and coefficient of variation (CV%) 2.75% due to the small residuals relative to the predicted value from the model. Figure 1 presents a plot of predicted versus actual RCO value. High value of R^2 (0.9918) shows the quadratic polynomial model adequately explain the data variation and represent the actual relationship between RCO response and the significant variables. This is strongly supported by the high value of adjusted R^2 (0.9841). On the other hand, predicted R^2 base on PRESS is in reasonable agreement with the adjusted R^2. The selected model explain about 96.28% of the variability in predicting new data as compared to the 99.18% of the variability in the original data. The overall predictive capability of the model is satisfied.

The model adequacy was further proved by checking on the validity of the assumption. The residual analysis plays an important role because residual is the difference between actual value of response and the predicted value from regression model [27]. To examine residuals in this study, Figure 2 shows a normal probability plot obtained from the residuals after fitting the quadratic polynomial model to the data. Figure 2 reveals that the model fitting is adequate and no outlier point in the data as the residuals plot lying approximately along the straight line, in which normality assumption is satisfied. Another diagnostic test to detect violations of the assumptions always shown by the plot of the residuals in each experimental point against the predicted response from corresponding experiment as Figure 3. The residuals scatter randomly in Figure 3 suggest that the variance of the actual RCO value is constant for all predicted RCO values. Therefore, the assumption of error with constant variance is satisfied and proved that the quadratic polynomial model in this study is adequate.

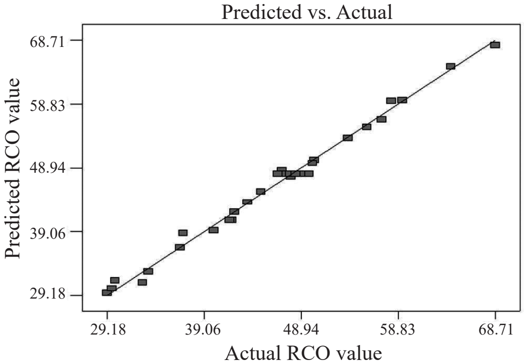


Figure 1: Predicted versus actual RCO.

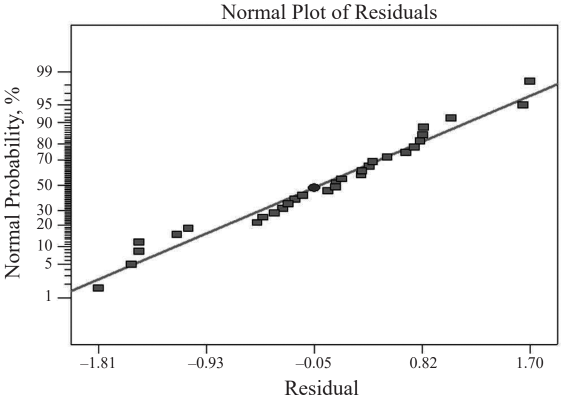


Figure 2: Normal probability plot of residuals.

According to the quadratic polynomial equation, predicted RCO values are plotted in the three-dimensional (3D) plots known as response surface plots and perform in contour plots. Therefore, it is easy to understand the relationships between independent variables and RCO responses. Significant interaction variables in the fitted quadratic polynomial model which analyse by ANOVA are chosen as axes for the response surface plots. Two independent variables are plotted at one time with another two variables set at constant (coded level = 0).

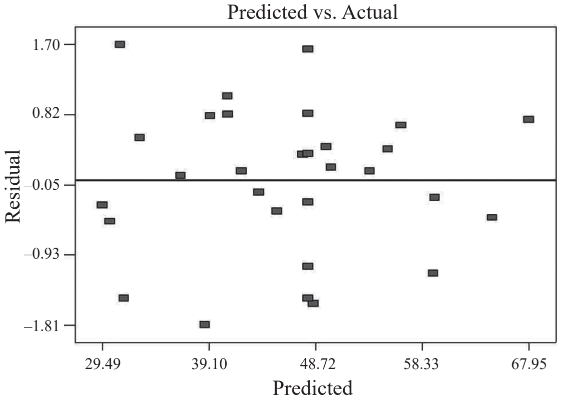
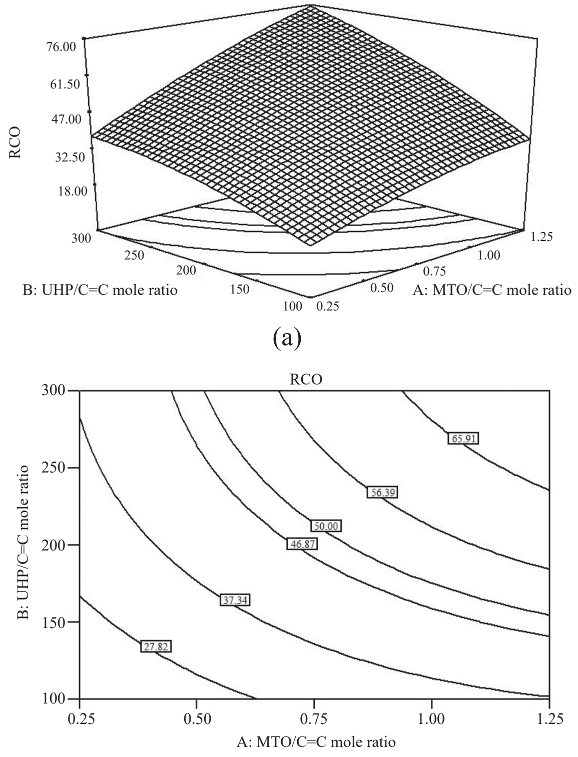


Figure 3: Plot of residuals against predicted RCO value in the catalytic partial epoxidation Response Surface plotting.

In this catalytic partial epoxidation, the cooperative relations between MTO and UHP proceed via a complexation reaction involving monoperoxorhenium and diperoxorhenium intermediates [9]. The presence of the peroxorhenium intermediates can be visually identified by the appearance of distinctive yellow colour in solution [25]. Peroxorhenium intermediates transfer the oxygen to double bond for the formation of oxirane ring. Therefore they are known as oxygen-transfer complexes. Figure 4(a) and (b) show the 3D and contour plot for the interaction effect between MTO (A) and UHP (B) on RCO values while the pyridine/C=C mole ratio (C) and reaction time (D) set at 9 mol% at reaction time of 120 min respectively. RCO values in percentage are increasing with MTO and UHP mole ratio. The larger increment of RCO values are obtained at higher mole ratio as compared to lower mole ratio. The result was ascribed to the increasing of monoperoxorhenium and diperoxorhenium intermediates formation and accelerated the reaction of epoxidation. On the other hand, RCO values were decreased at lower mole ratio of MTO and UHP. This result is in agreement with others study where the lower epoxidation degree was obtained when reducing both MTO and H_2O_2 proportions in the epoxidation of soybean oil [6]. Theoretically, partial epoxidation formed when the RCO value is 50%. Hence, it was noteworthy that MTO/C=C mole ratio higher than 0.50 mol% and UHP/C=C mole ratio higher than 150 mole% lead to the partial epoxidation within the range of the experiment conditions.

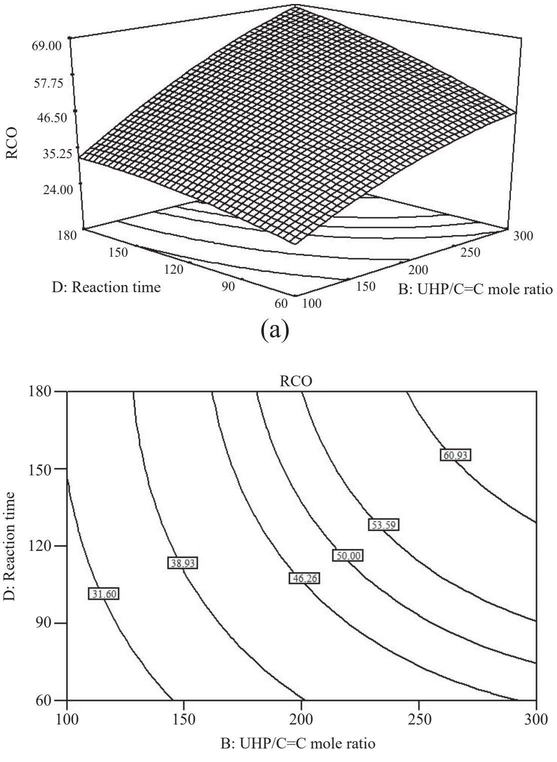


(a)

(b)

Figure 4: Response surface plot (a) and contour plot (b) for the effect of MTO (A) and UHP (B) on RCO values in catalytic partial epoxidation, pyridine/C=C mole ratio (C) = 9 mol% and reaction time (D) = 120 min.

Although the cooperative relations between MTO and UHP affect the RCO values, UHP is the main oxidant which restrict the formation of oxygen-transfer complexes [9]. Therefore, the effects of catalyst MTO (A) and reaction time (D) on RCO from ANOVA are not significant in the variability. On the other hand, the effect of UHP (B) and reaction time (D) contribute significantly on RCO response [Figure 5(a) and (b)]. The MTO/C = C mole ratio (A) and pyridine/C=C mole ratio (C) were kept constant at 0.75 and 9 mol% respectively. RCO values in percentage is increasing with UHP/C = C mole ratio and reaction time at the constant MTO/C = C mole ratio. However, RCO increase tremendously with UHP/C=C mole ratio as compared to reaction time due to the restrict formation of oxygen-transfer complexes by UHP. RCO values only increase gradually with reaction time particularly



(a)

(b)

Figure 5: Response surface plot (a) and contour plot (b) for the effect of UHP (B) and reaction time (D) on RCO values in catalytic partial epoxidation, pyridine/C = C mole ratio (C) = 9 mol% and MTO/C=C mole ratio (A) = 0.75 mol%.

at low level UHP. Indeed, Figure 5 support the fact that UHP is the main factor or variable in the epoxidation reaction to control the degree of epoxidation. Figure 5(b) indicates that partial epoxidation starts at the mole ratio of UHP higher than 150 mol% and reaction time longer than 60 min within the experimental conditions.

Pyridine is a Lewis base, transfers the MTO and peroxorhenium intermediates to the organic phase to ensure high epoxidation activity and increasing the rate of epoxidation [25]. In this study, the effect of pyridine showed less increment comparing with MTO and UHP in the constant reaction time thus pyridine with varying mole ratio to C = C is not significant variable. This result is in agreement with others where the epoxidation rate is independent of pyridine concentration, nevertheless the pyridine-free epoxidation rate is lower [9].

3.3 *Model verification and optimization of catalytic partially epoxidation*

The optimum conditions for MTO-catalysed partial epoxidation were predicted by Design-Expert software according to the quadratic polynomial model. The variables were set at the range from coded level –2 to +2 while the range for RCO response between 50% and 60% due to the formation of diepoxide. Table 5 shows the optimized conditions with the predicted and actual RCO values. Verification results revealed that the predicted RCO values were reasonably close to the actual values. In order to verify the optimized results, compositions of monoepoxide (ME) and diepoxide (DE) were analysed by the gas chromatography (Table 5). The composition of methyl linoleate monoepoxide is the total composition of the two isomers of the monoepoxide regio isomer. The GC-FID chromatogram of partial epoxidation showed two peaks that were not perfectly separated. Both peaks represented the methyl linoleate monoepoxide region isomers namely methyl 12,13-epoxy-9Z-octadecenoate and methyl 9,10-epoxy-12Z-octadecenoate. Both isomers had a ratio close to 1. The ratio implies that MTO is a nonspecific catalyst that cannot differentiate a double bond C = C during the epoxidation reaction. Unlike enzyme catalytic epoxidation, some monoepoxides were further converted to diepoxide before depletion of methyl linoleate in MTO catalytic epoxidation studies. The methyl linoleate diepoxide (methyl 9,10-12,13-diepoxytocecanoate) was also detected with two peaks. This is due to the presence of anti diastereomer and syn diepoxide having melting points at 78°C and 36°C. The diepoxide composition is also the sum of the two methyl linoleate diepoxides. Among these six optimised conditions, the best solution which showed the highest composition of monoepoxide (79.05%) at RCO 58.15% under condition of 0.75 mol% mole ratio of MTO, 300 mol% mole ratio of UHP, 9 mol% of pyridine at 120 min reaction time was chosen.

4 Conclusions

A partial epoxidation of methyl linolate reaction was successfully carried out at room temperature. The regression model from RSM has been successfully optimize the partial epoxidation of methyl linoleate for MTO-catalysed partial epoxidation method with

Table 5: Optimized conditions of catalytic partially epoxidation

MTO/C=C Mole Ratio (mol%)	UHP/C=C Mole Ratio (mol%)	Pyridine/C=C Mole Ratio (mol%)	Reaction Time (min)	Predicted RCO (%)	Actual RCO (%)	%ME[a]	%DE[b]
1.00	150	12	150	50.13	50.30	69.40	6.96
0.75	200	9	180	53.60	53.72	71.58	8.86
1.00	250	6	90	55.24	55.63	72.14	9.76
1.00	250	12	90	56.45	57.14	73.47	10.33
0.75	300	9	120	59.32	58.15	79.05	8.12
1.25	200	9	120	59.47	59.26	74.90	15.62

[a] Composition monoepoxide in percentage
[b] Composition diepoxide in percentage

high yields. The relationship between various variables was also successfully proved in the response surface and contour plots. It is found that controlled use of MTO catalyst quantities produce products/materials with different epoxidation degrees. The effect of UHP mole ratios is the dominant factor in the epoxidation followed by the mole ratio of MTO, reaction time and mole ratio of pyridine in order to control the degree of epoxidation.

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