Sains Malaysiana 47(7)(2018): 1359–1367
http://dx.doi.org/10.17576/jsm-2018-4707-02

The Optimization of RBD Palm Oil Epoxidation Process using D-Optimal Design

(Pengoptimuman Proses Pengepoksidaan Minyak Sawit RBD
menggunakan Reka Bentuk D-Optimum)

NURAZIRA MOHD NOR, DARFIZZI DERAWI & JUMAT SALIMON*

ABSTRACT

The epoxidation process of RBD palm oil was carried out using in situ *generated performic acid. The effect of various process variables such as the formic acid towards hydrogen peroxide mole ratio, the reaction temperature and the reaction time were optimized by using response surface methodology (RSM). The D-optimal design was used to evaluate the influence of process variables and their interaction in order to obtain the process optimum conditions. The results showed that the optimum conditions of the epoxidation process were at 5.91 mole ratio of formic acid towards 3.60 mole of hydrogen peroxide, reaction temperature of 40ºC and reaction time of 2.55 h. At the optimum condition, the epoxidised RBD palm oil (EPO) yield was 86% with oxirane oxygen content (OOC) of 3.46%. The results showed in good agreement with the predicted values from the RSM model.*

Keywords: D-optimal design; epoxidation; epoxidised RBD palm oil; optimization

ABSTRAK

Proses pengepoksidaan minyak sawit RBD telah dijalankan menggunakan asid performik terjana secara in-situ. *Kesan pelbagai proses pemboleh ubah seperti nisbah mol asid formik terhadap hidrogen peroksida, suhu tindak balas dan masa tindak balas telah dioptimumkan dengan menggunakan kaedah permukaan respons (RSM). Reka bentuk D-optimum telah digunakan untuk menilai pengaruh dan interaksi pelbagai pemboleh ubah proses untuk mendapatkan keadaan proses yang optimum. Keputusan kajian menunjukkan bahawa keadaan optimum proses pengepoksidaan diperoleh pada nisbah 5.91 mol asid formik terhadap 3.60 mol hidrogen peroksida, suhu tindak balas pada 40ºC dan masa tindak balas selama 2.55 jam. Pada keadaan optimum, hasil minyak sawit terepoksida (EPO) adalah sebanyak 86% dengan nilai kandungan oksigen oksiran (OOC) sebanyak 3.46%. Keputusan kajian menunjukkan keputusan yang menyamai nilai-nilai yang diramalkan daripada model RSM.*

Kata kunci: Minyak sawit RBD; pengepoksidaan; pengoptimuman; reka bentuk D-optimum

INTRODUCTION

Currently, plant oils based lubricant are increasingly used in lubricant industry to replace petrochemicals based lubricants due to their depletion at a faster rate, increasing cost of petrochemicals and rising concern for the environmental pollution (Borugadda & Goud 2015, 2014; Kotwal et al. 2013). It is due to plant oils are renewable resources, cheaper, biodegradable and non-toxic, compared to conventional source of petrochemicals. Plant oils itself exhibit good lubrication properties with high viscosity index (Nirmal & Dineshbabu 2015). However, plant oils have some drawbacks which will restrict their direct application as lubricant. One of the drawbacks is its low oxidative stabilty (Salimon et al. 2011; Wu et al. 2000) due to the presence of bis-allylic protons in plant oils structure which are highly susceptible to free radical attack and therefore undergoes oxidative degradation to form polar oxy compounds (Adhvaryu et al. 2005; Borugadda & Goud 2015; Erhan et al. 2006; Sharma et al. 2007; Singh & Chhibber 2013). The rate of the oxidation process can be attributed to the numbers of unsaturated fatty acids presence in its composition (Borugadda & Goud 2015, 2013).

This oxidative drawback that incur in the plant oils can be overcome by molecule structural redesign through the chemical modifications. The presence of the double bonds and its reactivity have allowed the functional addition reactions into the unsaturated fatty acids. The epoxidation process is one of the most important functionalization reactions of the double bond to other stable functional groups in order to improve the plant oils oxidative stability (Moser & Erhan 2007; Salimon et al. 2015, 2011). It is also the most widely industrial used process towards highly unsaturated plant oil to increase their industrial usage (El-Adly et al. 2014). Epoxidised plant oils products from the epoxidation process can be used as high-temperature lubricants (Lathi & Mattiasson 2007; Salimon et al. 2010), plasticizers (Joseph et al. 2014) and high temperature coating materials (Derawi & Salimon 2016). Recently, palm oil become one of the potential plant oils in order to produce biolubricant base stock (Salimon & Salih 2009; Salimon et al. 2015).

There are many studies reported on the epoxidation process of plant oils. Milchert and Smagowicz (2009) reported the epoxidation of rapeseed oil with peracetic acid. They studied the influence of reaction variables on the epoxidation of rapeseed oil by using conventional method of optimization. Kouroosh Saremi et al. (2012) also reported the epoxidation of soybean oil using formic acid and hidrogen peroxide. However, there are few studies reported on the epoxidation of palm oil. In 2014, Derawi et al. have discussed the synthesis of epoxidized palm olein by using different peroxy acids and its characterization. Furthermore, Hoang and Kim (2015) reported the effect of reaction time on epoxidation of palm oil. However, there are no report explained about the significant effect of reaction variables and interaction among the variables process in the optimization process of the epoxidation of palm oil using response surface methodology (RSM). This study is focused on the epoxidation of refined, bleached and deodorized palm oil (RBDPO). RBDPO which abundantly available all over Malaysia contains high percentage of unsaturated fatty acid (49.4%) (Njoku et al. 2010), which serve as good starting material for the epoxidation process. Figure 1 shows a proposed schematic reaction for the epoxidation of RBDPO represented by the structure of 1,3-dipalmitoyl-2-oleoyl-gliserol (POP) as the dominant triacylglycerol content (30.2%) in RBDPO.

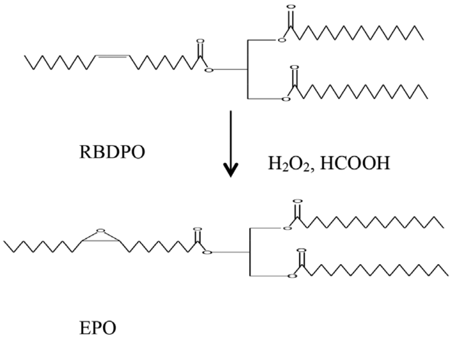


FIGURE 1. The schematic reaction for the epoxidation of RBD palm oil

Therefore, this study was conducted to understand the significant effect and important interaction among reaction variables towards the epoxidation of palm oil process in order to get the optimum conditions for highest yield of EPO with high oxygen oxirane content (OOC) value and low iodine value. The significant effect and the interaction among reaction variables will be explained by the analysis of variance (ANOVA) and 3-D response surface using D-optimal design.

MATERIALS AND METHODS

RBD palm oil was obtained from Sime Darby Jomalina, Teluk Panglima Garang, Selangor, Malaysia. Formic acid (88%) was obtained from Fisher Scientific and hydrogen peroxide (30 %) from Merck. Sodium hydrogen carbonate and sodium chloride were purchased from Systerm.

The epoxidation process was carried out using RBDPO and performic acid to prepare epoxidized palm oil (EPO). RBDPO was mixed with formic acid into 250 mL three necks round bottom flask equipped with mechanical stirrer, thermometer and reflux condenser. The mixture of RBDPO and formic acid were heated and continuously stirred (900 rpm) using a magnetic stirrer. Hydrogen peroxide was added slowly drop wise. The product, epoxidized palm oil (EPO) was neutralized with sodium hydrogen carbonate solution (5%), sodium chloride solution (5%) and distilled water. After the separation, the product (EPO) was kept for overnight by adding anhydrous sodium sulphate to remove water. The product was filtered using Whatmann No. 1 filter paper. The oxirane oxygen content (OOC %), yield (%) and iodine value (IV mg/g) were measured.

The epoxidation reaction was evaluated using D-optimal design mode. Table 1 shows the independent variables used in the study such as formic acid (HCOOH) mole (w/w, A), hydrogen peroxide (H_2O_2) mole (w/w, B), reaction temperature (^{o}C, C) and reaction time (h, D). Percentage of epoxide product, EPO (yield), oxirane oxygen content value (OOC) and iodin value (IV) were chosen as responses in this optimization. The mathematical relationship between the process variables and responses were calculated by quadratic polynomial equation (Borugadda & Goud 2015; Salimon et al. 2016):

$$Y = \beta_0 + \Sigma\, \beta_i x_i + \Sigma\, \beta_{ii} x_i^2 + \Sigma\Sigma\, \beta_{ij} x_{ixj} \qquad (1)$$

where β_0 ; β_i; β_{ii} and β_{ij} are constant, linear, square and interaction regression coefficient terms, respectively and x_i and x_j are independent variables (Razali et al. 2010; Salimon et al. 2016). Analysis of variance (ANOVA) was carried out to estimate the effects of process variables and their possible interaction effects on the higher yield and OOC and lower IV in the response surface regression procedure (Borugadda & Goud 2015; Salimon et al. 2016). The goodness and best fit of the model were evaluated by a regression coefficient R^2 (Borugadda & Goud 2015).

RESULTS AND DISCUSSION

D-optimal design was used to evaluate the optimization of epoxidation process of RBD palm oil. The optimum conditions of reaction were aimed at higher yield of EPO, higher oxirane oxygen content (OOC) and lower iodine value (IV). The quadratic polynomial equations were obtained from the experimental data to predict the optimal response as shown below in terms of coded variables:

$$\begin{aligned}\text{Yield (higher)} = {} & 84.61 - 1.54A + 1.29B - 0.42C + \\ & 0.41\,D - 12.20A^2 - 1.11B^2 + \\ & 0.71C^2 - 0.83D^2 - 1.19AB - \\ & 0.002553AC - 0.73AD + \\ & 0.19BC - 0.42\,BD - 0.12CD\end{aligned} \qquad (2)$$

TABLE 1. Independent variables and their levels for D-optimal design for epoxidation reaction

Independent variables	Symbol	Unit	Variable levels		
			-1	0	+1
HCOOH mole	A	mole	3	6	9
H_2O_2 mole	B	mole	1	2.5	4
Temperature	C	°C	40	47.5	55
Time	D	h	2	2.75	3.5

$$\text{IV (lower)} = -0.32 + 2.90A - 1.14B - 0.50C - 0.61D + 6.92A^2 + 1.17B^2 - 0.072C^2 + 1.03D^2 + 1.17AB + 1.06\,AC + 1.71AD - 0.072\,BC + 0.64\,BD + 0.18CD \quad (3)$$

$$\text{OOC (higher)} = 3.43 - 0.20A + 0.097B + 0.026C + 0.038\,D - 0.59\,A^2 - 0.077B^2 + 0.046C^2 - 0.087D^2 - 0.093AB - 0.067AC - 0.11AD - 0.014\,BC - 0.030BD - 0.017\,CD \quad (4)$$

ANOVA as a multivariate technique was studied to determine the optimum reaction conditions (Borugadda & Goud 2015). Tables 2, 3 and 4 summarize the analysis of variance (ANOVA) for all responses (yield, IV and OOC). The significance models are decided based on the P- value (Borugadda & Goud 2015; Tabrizi & Nassaj 2011). The P value less than 0.05 indicate model terms are significant. From the table, it can be seen that the P-value for all model responses were very small (<0.0001). This shows that the regression models for the data on all responses (yield, IV and OOC) were highly significant ($p<0.01$) with satisfactory R^2.

The significance of each variables can be seen in Tables 2, 3 and 4. The lower the P-value, the variable is more significant (Aziz et al. 2014). For EPO yield response, the linear term of A (mole of formic acid), B (mole of hydrogen peroxide) and C (temperature) were highly significant ($p<0.01$) and linear term of D (time) was significant ($p<0.05$). For IV response, all the linear term of A, B, C and D were highly significant ($p<0.01$). For OOC response, the linear term of A and B were highly significant ($p<0.01$) and linear term of C and D were significant ($p<0.05$). The results showed all reaction variables give significant values based on the low P-values ($p<0.05$). It means all reaction variables are important and give significant effect towards epoxidation in order to give the optimum conditions for high yield of epoxide, high OOC value and low IV.

The EPO yield response shows the quadratic term of A^2 and B^2 were highly significant ($p<0.01$). The quadratic term of A^2 was highly significant ($p<0.01$) for both IV and OOC responses. While the quadratic term of B^2 and D^2 were significant ($p<0.05$) for both IV and OOC responses. The yield response shows the interaction term of AB and AD were highly significant ($p<0.01$) and interaction term of BD was significant ($p<0.05$).

The significance of interaction among reaction variables also can be seen in Tables 2, 3 and 4. The EPO yield response shows the interaction term of AB and AD were highly significant ($p<0.01$) and interaction term of BD was significant ($p<0.05$). It shows interaction between mole of HCOOH (A) and mole of H_2O_2 (B), interaction between mole of HCOOH (A) and reaction time (D) and interaction between mole of H_2O_2 (B) and reaction time (D) were affected the epoxidation process in order to give higher yield of epoxide.

For both IV and OOC responses, the interaction term of AB, AC and AD were highly significant ($p<0.01$). While interaction term of BD was highly significant ($p<0.01$) for IV response and was significant ($p<0.05$) for OOC response. It shows all interactions between mole of HCOOH (A) and mole of H_2O_2 (B), interaction between mole of HCOOH (A) and reaction temperature (C), interaction between mole of HCOOH (A) and reaction time (D) and interaction between mole of H_2O_2 (B) and reaction time (D) were influenced the epoxidation process to give higher OOC value and lower IV. These results indicated there are some interaction between variables will affect the epoxidation process. This can be seen through their significant P-value ($p<0.05$). While the other interactions will not give effect on epoxidation based on their insignificant P-values. The significance interaction among the variables will be discussed later in 3-D response surfaces.

The precision of a model is judged by the regression coefficient (R^2). Regression coefficient R^2 represents that the accuracy and general ability of the polynomial model is good (Borugadda & Goud 2015). The R^2 value is always in between 0 and 1 and its order of magnitude suggests the aptness of the model (Borugadda & Goud 2015; Manivannan & Rajasimman 2011). For a good statistical model, the R^2 value should be close to one. The R^2 values for the yield, IV and OOC were 0.9974, 0.9942 and 0.9948, respectively (Tables 2, 3 & 4), which was close to 1 and it signifies that the 99.74%, 99.42% and 99.48% model behavior can be interpreted for optimum condition such as higher yield, lower IV and higher OOC, while only 0.26%, 0.58% and 0.52 % of the full variance each responses cannot be explained by the model.

The adjusted coefficient of determination (adj R^2) pointed to the goodness of the model (Aziz et al. 2014). The predicted R^2 value for yield (0.9796) was in reasonable agreement with the adjusted R^2 (0.9938) and the predicted

TABLE 2. Analysis of variance (ANOVA) for yield response

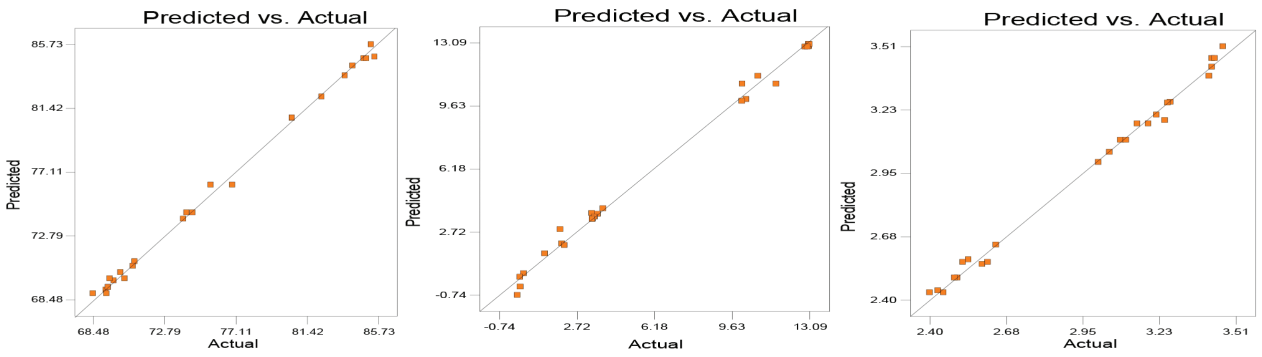
Source	Sum of squares	Df	Mean square	F-values	P-value
Model	981.34	14	70.10	277.12	< 0.0001
A-HCOOH mole	34.83	1	34.83	137.69	< 0.0001
B-H_2O_2 mole	25.28	1	25.28	99.96	< 0.0001
C-Temperature	2.62	1	2.62	10.35	0.0092
D-Time	2.07	1	2.07	8.19	0.0169
A^2	639.55	1	639.55	2528.44	< 0.0001
B^2	2.77	1	2.77	10.95	0.0079
C^2	1.10	1	1.10	4.36	0.0633
D^2	1.15	1	1.15	4.54	0.0590
AB	17.29	1	17.29	68.35	< 0.0001
AC	7.963E-005	1	7.963E-005	3.148E-004	0.9862
AD	6.28	1	6.28	24.82	0.0006
BC	0.41	1	0.41	1.63	0.2305
BD	2.20	1	2.20	8.71	0.0145
CD	0.17	1	0.17	0.66	0.4369
Residual	2.53	10	0.25		
Lack of fit	0.88	5	0.18	0.53	0.7474
Pure error	1.65	5	0.33		
Cor total	983.87	24			
R^2	0.9974		Pred R^2	0.9796	
Adj R^2	0.9938				

R^2 value for IV (0.9314) was in reasonable agreement with the adjusted R^2 (0.9862), as well as the predicted R^2 value for OOC (0.9393) was in reasonable agreement with the adjusted R^2 (0.9875). It recommends prominent correlational statistics between the remarked values and the predicted data (Borugadda & Goud 2015). Thus, the regression model provides an excellent explaination of the relationship between the independent process variables and the response variable (Borugadda & Goud 2015; Tabrizi & Nassaj 2011). The observed value was reasonably close to the predicted value as shown in Figure 2.

In order to ensure a thorough model fit, test for lack-of- fit need to be estimated. The lack- of- fit is an assessment of failure of a model to represent the data that cannot be reported by random error (Borugadda & Goud 2015; Tabrizi & Nassaj 2011). The P-value of lack of fit for all responses were not significant (p>0.05). The insignificant P-value of lack of fit for yield, IV and OOC were 0.7474, 0.2305 and 0.2415, respectively. This indicates that lack of fit was consideraby significant relative to the pure error and all the models predicted for the responses were adequate.

INFLUENCE OF PROCESS VARIABLES ON OPTIMUM RESPONSES

The effect of interaction among variables on epoxidation can be illustrate by using the 3-D response surfaces. The significant interaction variables in the fitted models (Tables 2, 3 and 4) were chosen as the axes (HCOOH mole A, H_2O_2 mole B, reaction temperature C and reaction time D) for the response surface plots.



(a) Yield (b) IV (c) OOC

FIGURE 2. The actual and predicted plot of a) yield b) IV c) OOC

TABLE 3. Analysis of variance (ANOVA) for IV response

Source	Sum of squares	Df	Mean square	F-values	P-value
Model	595.17	14	42.51	123.12	< 0.0001
A-HCOOH mole	123.83	1	123.83	358.65	< 0.0001
B-H_2O_2 mole	19.61	1	19.61	56.78	< 0.0001
C-Temperature	3.71	1	3.71	10.74	0.0083
D-Time	4.73	1	4.73	13.70	0.0041
A^2	205.56	1	205.56	595.36	< 0.0001
B^2	3.05	1	3.05	8.85	0.0139
C^2	0.011	1	0.011	0.033	0.8594
D^2	1.75	1	1.75	5.06	0.0481
AB	16.54	1	16.54	47.91	< 0.0001
AC	13.64	1	13.64	39.50	< 0.0001
AD	34.37	1	34.37	99.53	< 0.0001
BC	0.062	1	0.062	0.18	0.6814
BD	5.01	1	5.01	14.52	0.0034
CD	0.39	1	0.39	1.13	0.3118
Residual	3.45	10	0.35		
Lack of fit	2.31	5	0.46	2.01	0.2305
Pure error	1.15	5	0.23		
Cor total	598.62	24			
R^2	0.9942		Pred R^2	0.9314	
Adj R^2	0.9862				

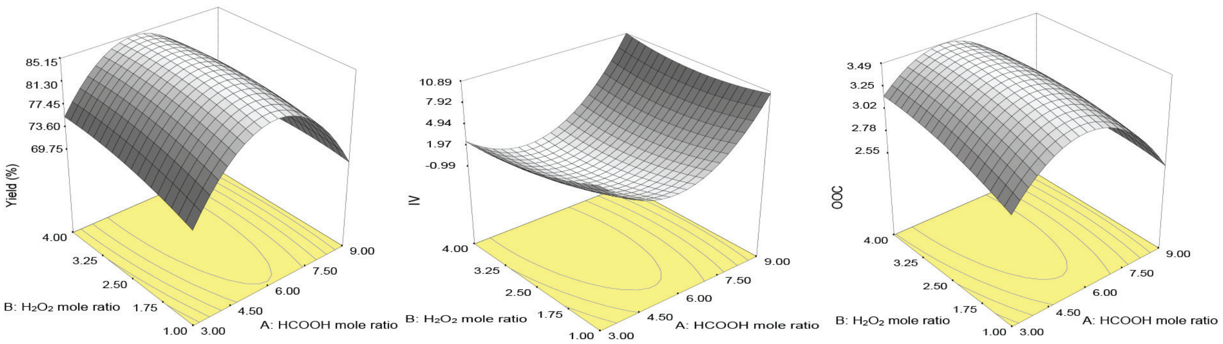
TABLE 4. Analysis of variance (ANOVA) for OOC response

Source	Sum of squares	Df	Mean square	F-values	P-value
Model	3.57	14	0.26	136.50	< 0.0001
A-HCOOH mole	0.61	1	0.61	326.47	< 0.0001
B-H_2O_2 mole	0.14	1	0.14	76.21	< 0.0001
C-Temperature	9.948E-003	1	9.948E-003	5.32	0.0438
D-Time	0.018	1	0.018	9.49	0.0116
A^2	1.51	1	1.51	806.63	< 0.0001
B^2	0.013	1	0.013	7.03	0.0242
C^2	4.676E-003	1	4.676E-003	2.50	0.1449
D^2	0.013	1	0.013	6.72	0.0269
AB	0.10	1	0.10	55.91	< 0.0001
AC	0.054	1	0.054	29.12	0.0003
AD	0.13	1	0.13	71.11	< 0.0001
BC	2.238E-003	1	2.238E-003	1.20	0.2996
BD	0.011	1	0.011	5.79	0.0369
CD	3.387E-003	1	3.387E-003	1.81	0.2081
Residual	0.019	10	1.870E-003	1.94	0.2415
Lack of fit	0.012	5	2.470E-003		
Pure error	6.350E-003	5	1.270E-003		
Cor total	3.59	24			
R^2	0.9948		Pred R^2	0.9393	
Adj R^2	0.9875				

The influence of mole of HCOOH (A) and mole of H_2O_2 (B) on yield, IV and OOC can be observed in Figure 3(a), 3(b) and 3(c). Increasing mole of HCOOH and H_2O_2 have increased the EPO yield and OOC. Higher values of yield and OOC were achived at 6 mole of HCOOH and 4 mole of H_2O_2. Increasing of H_2O_2 mole up to 4 has increased the OOC due to formation of more performic acid (Borugadda & Goud 2015). Increasing mole of HCOOH could increase OOC, but further increment of HCOOH mole would lead to a decline of OOC. Mole of HCOOH higher than 6 showed decreasing of both yield and OOC. HCOOH act as oxygen carrier and gets regenerated once the epoxidation reaction takes place (Mungroo et al. 2009). HCOOH also takes part in the overall reaction as a catalyst in the formation of oxirane ring and as a reactant in the hydrolysis of the oxirane ring (Goud et al. 2007, 2006). To attain the maximum oxirane oxygen content, the optimum level of the acid should be used where both the effects are balanced considering the amount of acid required in the formation of peracid (Goud et al. 2007, 2006). With high concentration of HCOOH, epoxy degradation may become crucial (Hoang & Kim 2015). Increasing of acid concentration has a detrimental effect on the oxirane ring. It is because oxirane ring was not stable in high HCOOH which acid promotes the hydrolysis of the epoxide, thereby decreasing the final OOC (Mungroo et al. 2008). Meanwhile, Figure 3(b) shows the IV decreased with an increase mole of HCOOH until 6 and increased with further increasing of HCOOH mole.

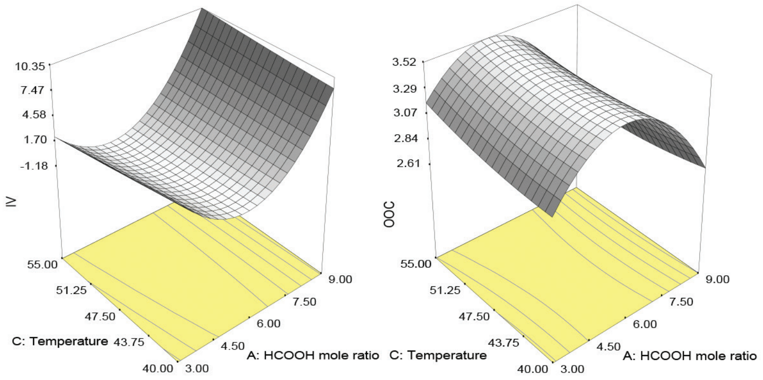
The effect of mole of HCOOH (A) and temperature (C) on IV and OOC can be observed in Figure 4(a) and 4(b). Increasing mole of HCOOH and temperature have increased the OOC value. OOC has maximum value at 6 mole of HCOOH and decreased with further increment of HCOOH mole until 9. It is due to excess HCOOH loading which leads to oxirane cleavage (Borugadda & Goud 2015; Dinda et al. 2008). Meanwhile, the IV has decreased with increasing HCOOH mole up to 6 and the value has increased with the further increment of HCOOH mole. The similar trend of response surface can be observed the affect of HCOOH mole (A) and time (D) on the EPO yield, IV and OOC as shown in Figure 5(a), 5(b) and 5(c).

Figure 6 shows the effect of various mole of H_2O_2 (B) and reaction time (D) on EPO yield, IV and OOC. Increasing mole of H_2O_2 and time have increased the yield and OOC. Higher values of yield and OOC were archived at 4 mole of H_2O_2 and 3.5 reaction time. Increasing of H_2O_2 mole up to 4 has increased the OOC due to formation of more performic acid (Borugadda & Goud 2015). But, the use of higher H_2O_2 mole must be avoided because it raised additional problem of agitation and decreases the mass transfer rate thereby decreases the OOC (Borugadda & Goud 2015). High concentration of H_2O_2 also will cause the epoxy group become unstable (Hoang & Kim 2015). Higher H_2O_2 will cause the stability of the oxirane ring become very poor (Goud et al. 2006) and it will lead to an accelerated rate of oxirane ring decomposition (Goud et



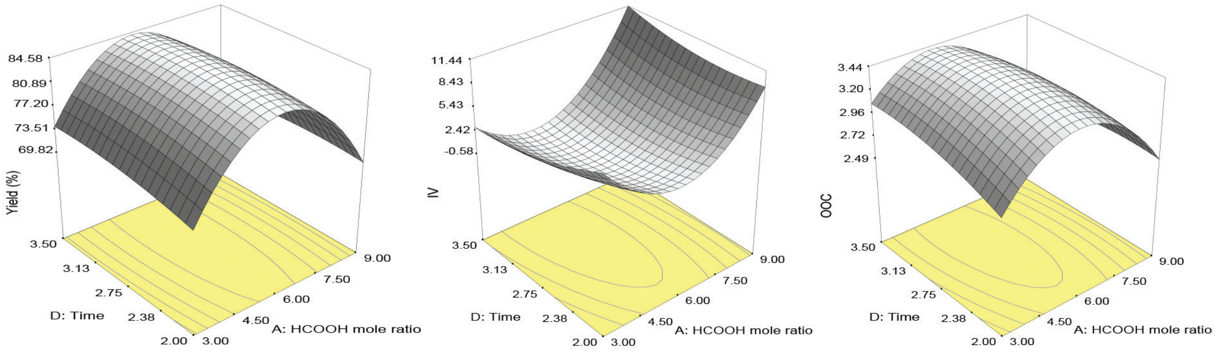
(a) Yield (b) IV (c) OOC

FIGURE 3. The effect of the HCOOH mole ratio and H_2O_2 mole ratio on a) yield, b) IV and c) OOC



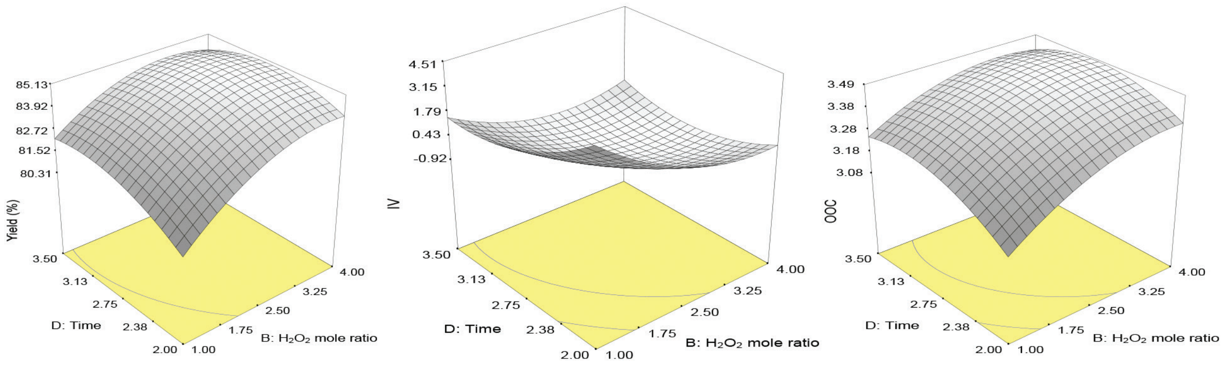
(a) IV (b) OOC

FIGURE 4. The effect of HCOOH mole ratio and temperature on a) IV and b) OOC



(a) Yield (b) IV (c) OOC

FIGURE 5. The effect of HCOOH mole ratio and time on a) yield, b) IV and (c) OOC



(a) Yield (b) IV (c) OOC

FIGURE 6. The effect of H_2O_2 mole ratio and time on a) yield, b) IV and (c) OOC

al. 2007). H_2O_2 act as oxygen donor in epoxidation. Higher concentration of peroxy acid must be avoided because epoxidation was exothermic process and it will lead to low stability of oxirane ring formed (Gunstone 2004). This condition also can be observed for reaction time. The increment of reaction time up to 3.5 h will increased the OOC. Further increase in reaction time will cause the decreasing of epoxidation due to the degradation of oxirane ring, production of more by product, water being formed and the undesirable oxirane ring opening reaction (Rafiee-Moghaddam et al. 2014). The higher H_2O_2 mole and higher reaction time provided an opportunity to react oxirane ring with excess H_2O_2, HCOOH and by-product water (Borugadda & Goud 2015; Suarez et al. 2009).

OPTIMUM CONDITION FOR EPOXIDATION OF RBDPO

The optimum conditions chosen from the solutions proposed by D-optimal design were 5.91 mole of HCOOH, 3.60 mole of H_2O_2, 40ºC reaction temperature and 2.55 h reaction time. The optimum value of responses that expected to obtain from these conditions are 85.86% yield, 0.07 mg/g IV and 3.48% OOC. These optimum conditions were tested three times in order to confirm the model prediction. The results obtained were 86% yield, 0.09 mg/g IV and 3.46% OOC with 99.14% of relative conversion oxirane (RCO) and these values were agree well with the predicted values from the model.

In this study, the optimization using D-optimal design has succeeded in producing optimum conditions that will give the best value of responses. The selection of the optimum conditions was affected by the interaction between all variables and criteria chosen for all responses. It shows that the D-optimal design optimization used in this study was very important because it takes into account all aspects compared to conventional method of optimization. The optimized conditions produce high percentage of epoxide product (86%) with the high percentage of relative conversion oxirane (99.14%). It means almost all unsaturated fatty acid in palm oil has been converted to oxirane ring in order to improve its oxidative stability.

CONCLUSION

The epoxidation process of RBDPO was successfully optimized using D-optimal design. The optimum reaction conditions were 5.91 mole of HCOOH, 3.60 mole of H_2O_2, 40ºC and 2.55 h. At this optimum conditions, the value of responses were 86% yield, 0.09 mg/g IV and 3.46% OOC with 99.14% of RCO. The significant effect and interaction among reaction variables were well explained by ANOVA and 3-D response surface. The results showed all variables have significant effect and there are some interactions between variables affect the epoxidation process, proved by their significant P-values. The optimized conditions have successfully produced high epoxide product with high OOC value as well as improved oxidative stabilty.

ACKNOWLEDGEMENTS

The authors are gratefully acknowledged to Universiti Kebangsaan Malaysia for financial support for research grant GUP-2016-012 and GUP-2016-058. The authors also thank the Ministry of Education, Malaysia for providing scholarship support (MyPHD) for the author.

REFERENCES

Adhvaryu, A., Liu, Z. & Erhan, S.Z. 2005. Synthesis of novel alkoxylated triacylglycerols and their lubricant base oil properties. *Ind. Crops Prod*. 21: 113-119.

Aziz, N.A.M., Yunus, R., Rashid, U. & Syam, A.M. 2014. Application of response surface methodology (RSM) for optimizing the palm-based pentaerythritol ester synthesis. *Industrial Crops and Products* 62: 305-312.

Borugadda, V.B. & Goud, V.V. 2015. Response surface methodology for optimization of bio lubricant basestock synthesis from high free fatty acids castor oil. *Energy Science & Engineering* 3(4): 371-383.

Borugadda, V.B. & Goud, V.V. 2014. Synthesis of waste cooking oil epoxide as a bio- lubricant base stock: Characterization and optimization study. *J. Bioproc. Eng. Bioref*. 3: 57-72.

Borugadda, V.B. & Goud, V.V. 2013. Comparative studies of thermal, oxidative and low temperature properties of waste cooking oil and castor oil. *J. Renew. Sustain. Energy* 5: 063104.

Derawi, D. & Salimon, J. 2016. Sintesis sebatian hidroksi-eter minyak sawit olein. *Sains Malaysiana* 45(5): 817-823.

Derawi, D., Salimon, J. & Ahmed, W.A. 2014. Preparation of epoxidized palm olein as renewable material by using peroxy acids. *The Malaysian Journal of Analytical Sciences* 18(3): 584-591.

Dinda, S., Patwardhan, A.V., Goud, V.V. & Pradhan, N.C. 2008. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalysed by liquid inorganic acids. *Bioresour. Technol*. 99: 3737-3744.

El-Adly, R.A., Shoaib, A.M., Enas, A.I. & Modather, F. 2014. Optimum operating conditions for epoxidation reaction of Jojoba and castor oils. *Int. Journal of Engineering Research and Applications* 4(3): 816-822.

Erhan, S.Z., Sharma, B.K. & Perez, J.M. 2006. Oxidation and low temperature stability of vegetable oil-based lubricants. *Ind. Crops Prod*. 24: 292-299.

Goud, V.V., Patwardhan, A.V., Dinda, S. & Pradhan, N.C. 2007. Kinetics of epoxidation of *Jatropha* oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chemical Engineering Science* 62: 4065-4076.

Goud, V.V., Patwardhan, A.V. & Pradhan, N.C. 2006. Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide. *Bioresource Technology* 97: 1365-1371.

Gunstone, F.D. 2004. *The Chemistry of Oils and Fats: Sources, Composition Properties and Uses*. London: Blackwell Publishing Ltd.

Hoang, T.T.K. & Kim, II. 2015. Epoxidation and ring-opening of palm oil to produce high functionality polyols. *Australia Journal of Basic and Applied Sciences* 9(8): 89-93.

Joseph, R., Madhusoodhanan, K.N., Alex, R., Varghese, S., George, K.E. & Kuriakose, B. 2014. Studies on epoxidised rubber seed oil as secondary plasticiser/stabiliser for polyvinyl chloride. *Plastics Rubber and Composites* 33(5): 217-222.

Kotwal, M., Kumar, A. & Darbha, S. 2013. Three- dimensional, mesoporous titanosilicates as catalysts for producing biodiesel and biolubricants. *J. Mol. Catal. A. Chem*. 377: 65-73.

Lathi, P.S. & Mattiasson, B. 2007. Green approach for the preparation of biodegradable lubricant base stock from epoxidised vegetable oil. *Applied Catalysis B: Environmental* 69: 207-212.

Manivannan, P. & Rajasimman, M. 2011.Optimization of process parameters for the osmotic dehydration of beetroot in sugar solution. *J. Food Process Eng*. 34: 804-825.

Milchert, E. & Smagowicz, A. 2009. The influence of reaction parameters on the epoxidation of rapeseed oil with peracetic acid. *J. Am. Oil Chem. Soc*. 86: 1227-1233.

Moser, B.R. & Erhan, S.Z. 2007. Preparation and evaluation of a series of α-hydroxy ethers from 9, 10-Epoxystreates. *Eur. J. Lipid Sci. Technol*. 109: 206-213.

Mungroo, R., Pradhan, N.C., Goud, V.V. & Dalai, A.K. 2008. Epoxidation of canola oil with hydrogen peroxide catalyzed by acidic ion exchange resin. *J. Am. Oil Chem. Soc*. 85: 887-896.

Nirmal, V.P. & Dineshbabu, D. 2015. Performance and emission of *Pongamia pinnata* oil as a lubricant in diesel engine. *International Journal of Innovative Research in Science, Engineering and Technology* 4(2): 435-441.

Njoku, P.C., Egbukole, M.O. & Enenebeaku, C.K. 2010. Physio-chemical characteristics and dietary metal levels of oil from *Elaeis guineensis* species. *Pakistan Journal of Nutrition* 9(2): 137-140.

Rafiee-Moghaddam, R., Salimon, J., Jelas-Haron, M.D., Jahangirian, H., Shah Ismail, M.H., Hosseini, S. & Rezayi, M. 2014. Lipase epoxidation optimizing of *Jatropha curcas* oil using perlauric acid. *Digest Journal of Nanomaterials and Biostructures* 9(3): 1159-1169.

Razali, N., Mootabadi, H., Salamatinia, B., Lee, K.T. & Abdullah, A.Z. 2010. Optimization of process parameters for alkaline-catalysed transesterification of palm oil using response surface methodology. *Sains Malaysiana* 39(5): 805-809.

Salimon, J., Abdullah, B.M. & Salih, N. 2016. Optimization of the oxirane ring opening reaction in biolubricant base oil production. *Arabian Journal of Chemistry* 9: 1053-1058.

Salimon, J., Ahmed, W.A., Salih, N., Yarmo, M.A. & Derawi, D. 2015. Lubricity and tribological properties of dicarboxylic acids and oleyl alcohol based esters. *Sains Malaysiana* 44(3): 405-412.

Salimon, J., Salih, N. & Yousif, E. 2011. Chemically modified biolubricant basestocks from epoxidized oleic acid: Improved low temperature properties and oxidative stability. *Journal of Saudi Chemical Society* 15: 195-201.

Salimon, J., Dina Azleema, M.N., Nazriwati, A.T., Mohd Firdaus, M.Y. & Noraisah, A. 2010. Fatty acid composition and physicochemical properties of Malaysian castor bean *Ricinus communis* L. seed oil. *Sains Malaysiana* 39(5): 761-764.

Salimon, J. & Salih, N. 2009. Substituted esters of octadecanoic acid as potential biolubricants. *European Journal of Scientific Research* 31(2): 273-279.

Saremi, K., Tabarsa, T., Shakeri, A. & Babanalbandi, A. 2012. Epoxidation of soybean oil. *Annals of Biological Research* 3(9): 4254-4258.

Sharma, B.K., Perez, J.M. & Erhan, S.Z. 2007. Soybean oil-based lubricants: A search for synergistic antioxidants. *Energy Fuel*s 21: 2408-2414.

Singh, C.P. & Chhibber, V.K. 2013. Chemical modification in karanja oil for biolubricant industrial applications. *J. Drug Deliv. Therapeutic*s 3: 117-122.

Suarez, P.A.Z., Perreira, M.S.C., Doll, K.M., Sharma, B.K. & Erhan, S.Z. 2009. Epoxidation of ethyl oleate using heterogeneous catalyst. *Ind. Eng. Chem. Res*. 48: 3268-3270.

Tabrizi, S.A.H. & Nassaj, E.T. 2011. Modeling and optimization of densification of nanocrystalline Al_2O_3 powder prepared by a sol–gel method using response surface methodology. *J. Sol-Gel. Sci. Technol*. 57: 212-220.

Wu, X., Zhang, X., Yang, S., Chen, H. & Wang, D. 2000. The study of epoxidized rapeseed oil used as a potential biodegradable lubricant. *JAOCS* 77: 561-563.

School of Chemical Science and Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: jumat@ukm.edu.my

Received: 5 August 2017
Accepted: 25 February 2018