Experimental Design using Response Surface Methods for Palm Olein-Based Hydroxy-Ether Systhesis
(Reka Bentuk Eksperimen menggunakan Kaedah Respons Permukaan untuk Sintesis Hidroksi-Eter Minyak Sawit Olein)

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ABSTRACT

Hydroxy-ether-PO$_o$ was synthesised via alcoholysis reaction of epoxidized palm olein (EPO$_o$). The experimental design was conducted using response surface methodology (RSM) based on 3 factors; reaction time, reaction temperature and catalyst loading. Responses such as percentage of conversion and percentage of yield were determined using statistical software 'Design Expert 9'. Hydroxy-ether-PO$_o$ showed the presence of proton peak attached to the carbon of ether (3.2, 3.5 ppm) and proton of the hydroxyl (4.8 ppm). The presence of carbon peak bonded to hydroxyl was detected at chemical shift 75 ppm and carbonyl carbon of ether at 72 ppm.

Keywords: Alcoholysis; oxirane cleavage; palm olein; response surface methods

ABSTRAK

Sebatian hidroksi-eter-PO$_o$ disintesis melalui tindak balas alkoholisis minyak sawit olein terepoksida (EPO$_o$). Reka bentuk eksperimen dirangka menggunakan kaedah respons permukaan (RSM) berdasarkan 3 faktor; masa tindak balas, suhu tindak balas dan peratusan mangkin. Respons peratusan penukaran dan peratus hasil tindak balas ditentukan menggunakan perisian statistik 'Design Expert 9'. Hidroksi-eter-PO$_o$ telah menunjukkan kehadiran puncak proton pada karbon eter (3.2, 3.5 ppm) dan proton pada kumpulan hidroksil (4.8 ppm). Puncak karbon hidroksi-eter-PO$_o$ yang terikat dengan kumpulan hidroksil dikesan pada anjakan kimia 75 ppm dan karbon pada karbonil kumpulan eter pada 72 ppm.

Kata kunci: Alkoholisis; kaedah respons permukaan; minyak sawit olein; pembukaan gelang oksirana

INTRODUCTION

Nowadays, world focus on the utilization of renewable sources as raw materials for chemicals production and industrial applications. In the past, these chemicals production were merely based on petroleum. With the current unstable world market price of crude petroleum and the increasing global temperature, renewable resources have been utilized as the alternative for petrochemical derivatives (Huang & Zhang 2002; Rozman et al. 2003; Velayutham et al. 2009). These resources are mostly obtained from plant oils for their versatility and for being environmentally-friendly and renewable (Xia & Larock 2010). Plant oils are biodegradable and do not pollute the environment (Biermann et al. 2000).

An example of a popular bio-based chemical compound derivative is epoxidized oil. A variety of epoxidized oil has been produced. These epoxidized oils were used as intermediate products to manufacture diversifying end products that were useful for industrial uses (Dinda et al. 2008; Goud et al. 2006; Jia et al. 2011; Meyer et al. 2008; Milchert & Smagowicz 2008). The oxirane ring on epoxidized oils could react with alcohol compounds through alcoholysis and generates a compound with the hydroxyl and ether group, as can be seen in Figure 1. The oxirane ring-opening reaction by alcohol substances

with acid catalysts depends upon the type of alcohol used (Wade 2006).

Malaysia is one of the world's largest producers of crude palm oil (CPO) and this has given the upper hand for Malaysia to develop its industrial commodities based on palm olein (PO$_o$). PO$_o$ consists of 31% oleic acid and 12% linoleic acid on its triglycerol chain (TAG) with iodine value between 51 and 61 (Gunstone 2004; O'Brien 1998; Scrimgeour 2005). Both acids in the PO$_o$ are essential for the modification of the TAG structure to generate a new substance as both were occupied with a double bond functionality, of which will be involved in the alteration of functional groups on the TAG ester chain. Thus, epoxidized palm olein (EPO$_o$) is desirable to be used in the modification process to synthesize a new hydroxy-ether palm olein substance (hydroxy-ether-PO$_o$). Since the establishment of utilizing bio-based resources, the EPO$_o$ oxirane ring-opening process through alcoholysis with moderate chain fatty acids has not been investigated. Although a few studies on the alcoholysis of other epoxide substances revealed some important findings. Erhan and Perez (2002) and Hwang and Erhan (2001) performed alcoholysis with acid sulphuric catalyst and studied the kinetics of the reaction. It was reported that the reaction kinetic was influenced by the type of
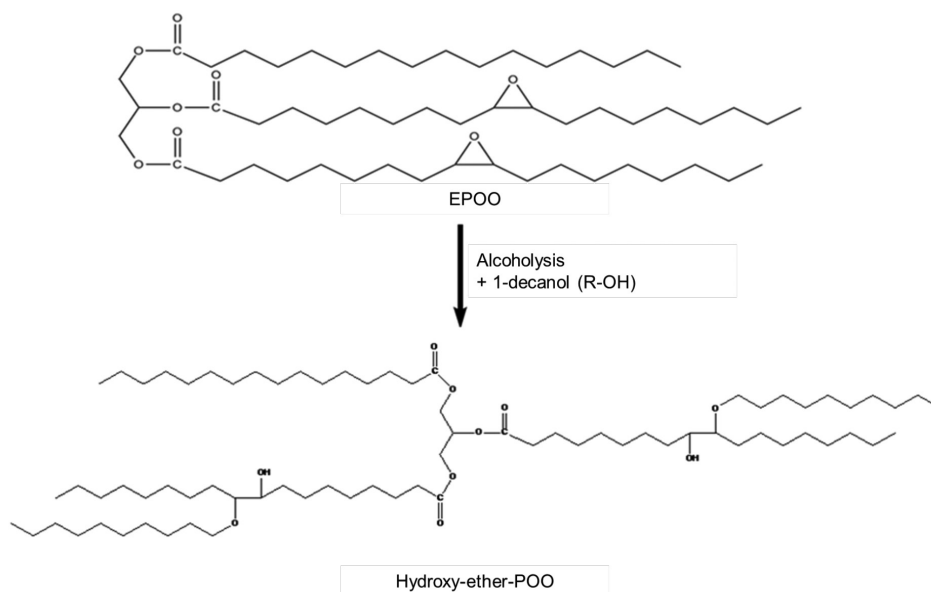
FIGURE 1. Alcoholysis reaction of EPO_o (EPOO is a major compound of EPO_o)

alcohol involved; methanol, 2-ethylhexanol, butanol, cyclohexanol and decanol. Alcoholysis by alcohols of more complex molecular structure and a longer chain produced lower reaction kinetics than a short-chained alcohol. Campanella et al. (2010) performed oxirane cleavage on epoxidized soybean oil (ESBO) by methanol and ethanol, generated methoxylated and etoxylated substances with fluoroboric acid (HBF_4) as the acid catalyst, adapting the methodology by Guo et al. (2000). Another set of study on ESBO alcoholysis was carried out by Guerbet (C12, C14, C16, C18), of which had used sulphuric acid (Hwang & Erhan 2006). Lin et al. (2008) studied the reaction kinetic of oxirane ring-opening on ESBO by methanol without introducing any catalyst, but manipulating the reaction temperature at 50, 60, 65 and 70°C. The research produced methoxylated polyols.

This paper discusses on the experimental design using statistical software Design Expert 9 to predict the percentage of conversion and yield based on 3 main factors; reaction time, reaction temperature and catalyst loading. The confirmatory tests used a carbon and proton nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR) (Pavia et al. 2001).

MATERIALS AND METHODS

Epoxidized palm olein (EPO_o) with 3.6% of oxygen oxirane content was prepared from palm olein (Seri Murni brand, FFM Marketing Sdn. Bhd.) (Darfizzi & Jumat 2010). 1-Decanol was supplied by Emery Oleochemicals (M) Sdn. Bhd.

Alcoholysis of EPO_o was performed using acid catalyst to produce hydroxy-ether-PO_o as Figure 1. Response surface analysis of alcoholysis reaction was designed using a statistical software; Design Expert 9 based on 3 factors; A: reaction time, B: reaction temperature and C: catalyst loading. Responses on percentage of conversion and yield were predicted using the software.

The chemical structure of product was evaluated with proton and carbon Nuclear Magnetic Resonance (^{13}C-NMR, ^{1}H-NMR) using FT-NMR 600 MHz Cryoprobe, Bruker Avance 111 600 MHz with chloroform as solvent ($CDCl_3$) (Darfizzi & Jumat 2013).

RESULTS AND DISCUSSION

CONVERSION ANALYSIS

Analysis of variance (ANOVA) for response surface linear model is shown as Table 1. The *Model F-value* of 5.43 implies the model is significant (Table 1). There is only a 1.21% chance that an *F-value* this large could occur due to noise. Values of F less than 0.0500 indicate model terms were significant. In this case, B and C were significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The *Lack of Fit F-value* of 2.17 implies the *Lack of Fit* was not significant relative to the pure error. There was a 23.65% chance that a *Lack of Fit F-value* this large could occur due to noise. Non-significant lack of fit is good.

The '*Pred R-Squared*' of 0.2483 is not as close to the '*Adj R-Squared*' of 0.4540 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider were model reduction, response transformation and outliers. All empirical models should be tested by confirmation runs. '*Adeq Precision*' measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 7.819 indicates an adequate signal. This model can be used to navigate the design space. The final equation in terms of coded factors as below:

TABLE 1. ANOVA for response surface linear model of conversion

Source	Sum of squares	df	Mean square	F Value	p-value Prob > F	
Model	830.37	3	276.79	5.43	0.0121	significant
A-Reaction Time	*97.37*	*1*	*97.37*	*1.91*	*0.1901*	
B-Reaction Temperature	*382.40*	*1*	*382.40*	*7.51*	*0.0169*	
C-Catalyst Loading	*350.60*	*1*	*350.60*	*6.88*	*0.0210*	
Residual	662.15	13	50.93			
Lack of Fit	549.70	9	61.08	2.17	0.2365	not significant
Pure Error	*112.44*	*4*	*28.11*			
Cor Total	1492.51	16				

Conversion = 83.98 + (3.49*A) + (6.91*B) + (6.62*C)　　(1)

Equation (1) in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors were coded as +1 and the low levels of the factors were coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Figure 2 represents the 3D surface graph of alcoholysis conversion while Figure 3 represents the predicted vs. actual value of conversion.

PERCENTAGE OF YIELD

Analysis of variance (ANOVA) for response surface quadratic model is shown as Table 2. The *Model F-value* of 11.15 implies the model is significant (Table 2). There is only a 0.22% chance that an *F-value* this large could occur due to noise. Values of F less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC,
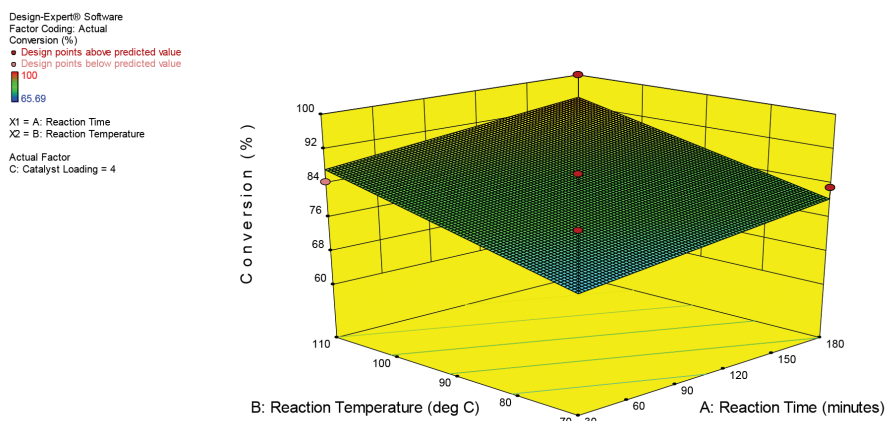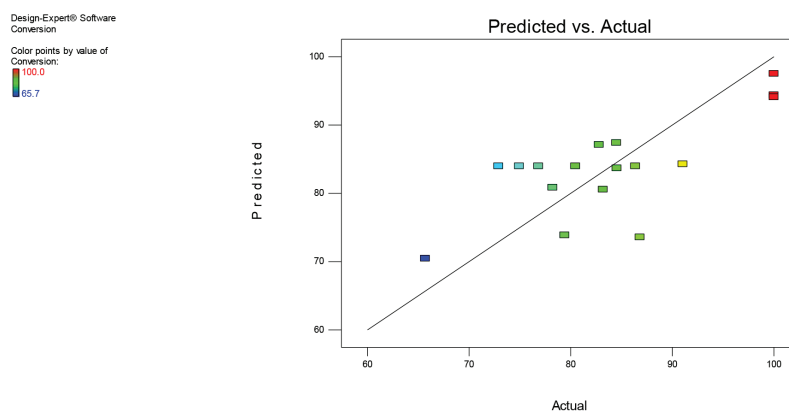

FIGURE 2. Conversion of alcoholysis reaction

FIGURE 3. Predicted vs. actual graph

TABLE 2. ANOVA for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	955.73	9	106.19	11.15	0.0022	significant
A-Reaction Time	57.35	1	57.35	6.02	0.0439	
B-Reaction Temperature	122.46	1	122.46	12.85	0.0089	
C-Catalyst Loading	297.68	1	297.68	31.24	0.0008	
AB	109.83	1	109.83	11.53	0.0115	
AC	130.42	1	130.42	13.69	0.0077	
BC	111.51	1	111.51	11.70	0.0111	
A^2	81.48	1	81.48	8.55	0.0222	
B^2	38.63	1	38.63	4.05	0.0839	
C^2	1.40	1	1.40	0.15	0.7131	
Residual	66.69	7	9.53			
Lack of Fit	5.60	3	1.87	0.12	0.9423	not significant
Pure Error	61.09	4	15.27			
Cor Total	1022.42	16				

BC, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms were not significant. The *Lack of Fit F-value* of 0.12 implies the *Lack of Fit* was not significant relative to the pure error. There is a 94.23% chance that a *Lack of Fit F-value* this large could occur due to noise. Non-significant lack of fit is good.

The '*Pred R-Squared*' of 0.8190 is in reasonable agreement with the '*Adj R-Squared*' of 0.8509; i.e. the difference is less than 0.2. '*Adeq Precision*' measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 10.378 indicates an adequate signal. This model can be used to navigate the design space. The final equation in terms of coded factors as below:

$$Yield = 81.56 + (2.68*A) + (3.91*B) + (6.10*C) + (5.24*AB) + (5.71*AC) + (5.28*BC) + (4.40*A^2) + (3.03*B^2) + (-0.58*C^2)$$

(2)

Equation (2) in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors were coded as +1 and the low levels of the factors were coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. Figure 4 represented the 3D surface graph of alcoholysis conversion while Figure 5 represented the predicted vs. actual value of conversion.

PROTON AND CARBON SPECTRA

Figures 6 and 7 show the comparison of proton and carbon spectra between hydroxy-ether-PO$_o$ and EPO$_o$. Both spectra proved the oxirane ring cleavage will happened after alcoholysis reaction performed to produce hydroxyl and ether functional groups. Chemical shift for proton attached to carbon which attached to hydroxyl group was detected at
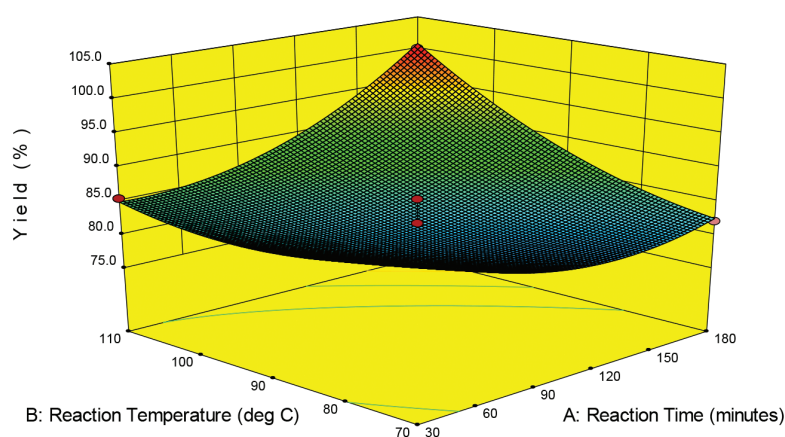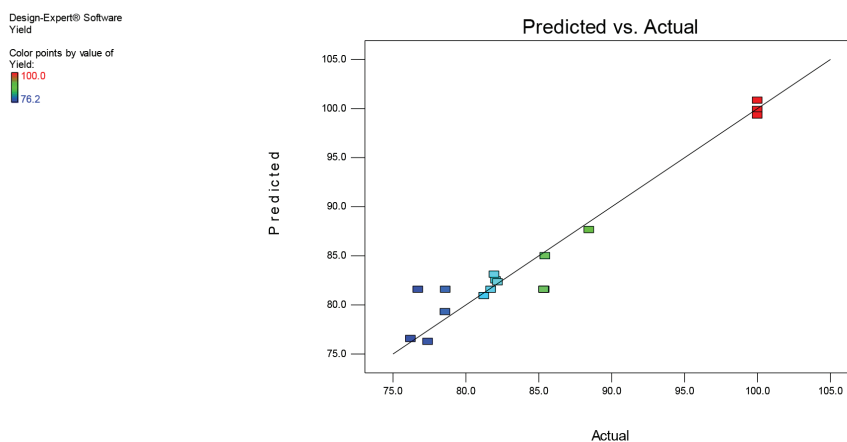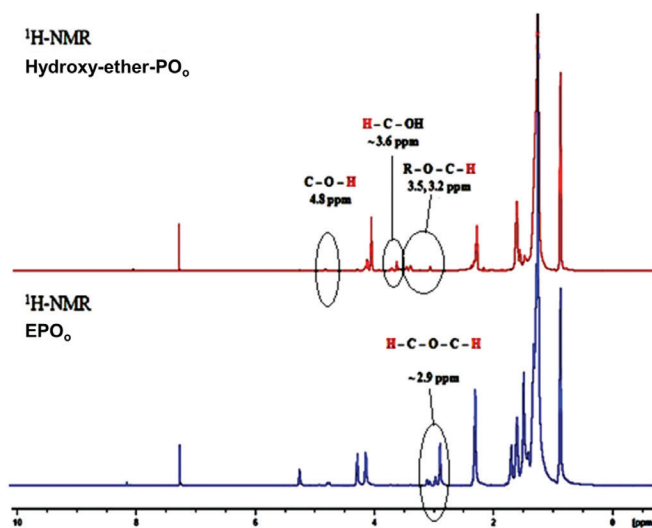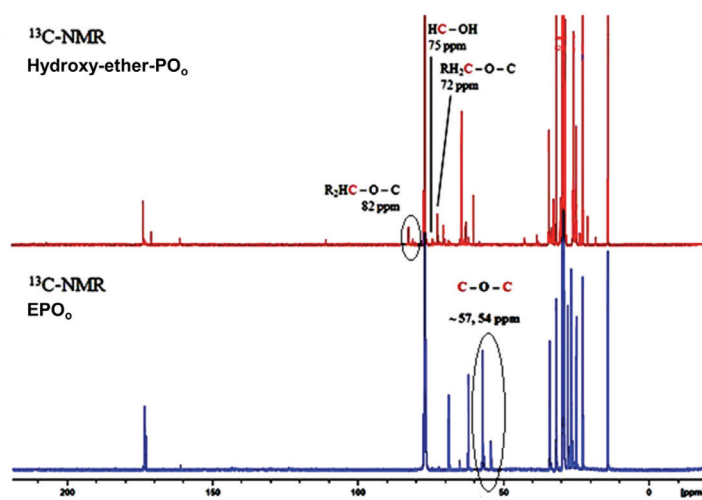

FIGURE 4. Percentage of yield of hydroxy-ether-PO$_o$

FIGURE 5. Percentage of yield of hydroxy-ether-PO$_o$

FIGURE 6. Comparison between ^{1}H-NMR spectrum of hydroxy-ether-PO$_o$ and EPO$_o$

FIGURE 7. Comparison between ^{13}C-NMR spectrum of hydroxy-ether-PO$_o$ and EPO$_o$

3.6 ppm and chemical shift for carbon attached to hydroxyl group detected at 75 ppm. Meanwhile, chemical shift for proton attached to ether group was detected at 3.2 and 3.5 ppm. Chemical shift for carbon of ether was detected at 82 ppm.

CONCLUSION

The alcoholysis reaction was successfully designed by Design Expert 9 and the reaction product has been fully characterised using proton and carbon analysis technique. Hydroxy-ether-PO$_o$ substances are very promising as the intermediate product for the studies on lubricant base stocks.

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