

# Optimization of Process Parameters for Diesters Biolubricant using D-optimal Design

Bashar Mudhaffar Abdullah and Jumat Salimon

**Abstract**—Optimization study of the diesters biolubricant oleyl 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate (OLHYOOT) was synthesized in the presence of sulfuric acid (SA) as catalyst has been done. Optimum conditions of the experiment to obtain high yield% of OLHYOOT were predicted at ratio of OL/HYOOA of 1:1 g/g, ratio of SA/HYOOA of 0.20:1 g/g, reaction temperature 110 °C and 4.5 h of reaction time. At this condition, the Yield% of OLHYOOT was 88.7. Disappearance of carboxylic acid (C=O) peak has observed by FTIR with appearance ester (C=O) at 1738 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra analyses confirmed the result of OLHYOOT with appearance ester (-CHOCOR) at 4.05ppm and also the <sup>13</sup>C-NMR confirmed the result with appearance ester (C=O) peak at 173.93ppm.

**Keywords**—Esterification, Diesters, Biolubricant, D-optimal design.

## I. INTRODUCTION

OLEOCHEMICALS that are derived principally from natural feeds tocks are referred to as natural oleochemicals [1]. Raw materials for most natural oleochemicals are tallow, tall oil, and vegetable oils. Oleochemical products may be classified as fatty acids, fatty alcohols, and glycerine [2]. Industrially, most fatty acids are obtained directly from animal or vegetable sources, resulting in fatty acids with linear even-numbered carbon chains. It is possible to produce various industrial products from fatty acids. Fatty acid products have important applications as solvents, plasticizers, resins, plastics, coatings, perfumes, flavors, cosmetics, soaps, medicinals, biofuels, and biolubricants [3].

Today, technology is available for high-quality synthetic lubricating oils. Synthetic lubricating oils based on renewable sources are important in developing environmentally acceptable lubricating oil alternatives. Lubricants being the predominant form of lubrication for machinery generally consist of base oil and additives. The lubricants in use today are petroleum-based. Environmental pollution associated with the production and applications of this huge quantity of lubricants worldwide are causing environmental concern. Currently, the lubricants sold worldwide end up in the environment via total loss applications, spills or major accidents [4, 5].

In view of its high ecological toxicity and low biodegradability it poses a considerable threat to the environment. In the last decade a lot of interest was developed to use environment friendly readily biodegradable lubricant fluids [5]. Depletion of world petroleum reserves and uncertainty in petroleum supply also stimulated the search for environmental friendly alternative to mineral oils [6, 7]. Today, around 2% of the base stocks are of vegetable oil origin [8]. The use of environmentally acceptable vegetable oil-based product as lubricants has many advantages. They are nontoxic, biodegradable, derive from renewable resource, and have a reasonable cost when compared to other synthetic fluids [9].

Recently, modern technological approaches have been adopted to solve the problems associated with application of vegetable oils in lubricants, and some of them are genetic modification, additive treatment and chemical modification [10]. However, low resistance to oxidative degradation still remains the major drawback of plant oil application in the lubricants [8]. There has been slow percolation of the product technologies developed in the European and American countries to the Asian countries [11].

Esters are known as natural lubricating oils. Besides being used as lubricants like other ester types (diesters, trimellitate esters, dimer acid esters, phthalate esters, and polyols), fatty acid esters can also be evaluated as synthetic lubricating oils. Before the early 1800s, the main lubricants were natural esters contained in animal fats or in vegetable oils. During World War II, a range of synthetic lubricating oils was developed [9].

In the field of the chemical modification of fatty acids to fatty esters of mono-alcohols, it is esterification of fatty acids by various mono-alcohols including methanol, propanol, butanol, oleyl alcohol, oleyl alcohol and stearyl alcohol, which is generally described in the literature to produce corresponding fatty esters [12]. The monoesters of mono-alcohols are fluid liquids or solid waxes. They are used as solvents in cosmetics or lubricants in metal treatment, textile industry, plastics industry. Esterification is usually catalyzed by an acid catalyst donor of protons such as sulfuric acid (SA) or by a metallic catalyst [13].

In this study, it presents a novel synthetic approach for esterification reaction of 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoic acid (HYOOA) with oleyl alcohol (OL) catalyzed by sulfuric acid (SA) (Fig. 1) was investigated as a lubricating oil candidate to improve the physical properties of biolubricants product such as low temperature (pour pint), flash point, viscosity and oxidative stability. In this study, the esterification product of HYOOA with OL was presented as lubricating oil for the first time. The objective of this study

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was to optimize process variables of esterification reaction. The process variables studied using D-optimal design were ratio of OL/HYOOA (g), ratio of SA/HYOOA (g), reaction temperature ( $^{\circ}\text{C}$ ) and reaction time (h). RSM was applied to relate these four process variables with the response (diesters biolubricant yield%).

## II. METHODOLOGY

### A. Experimental Procedure

The esterification reaction was carried out using OL and SA as catalyst [13]. Table I shows the different ratio of OL/HYOOA (g/g), different ratio of SA/HYOOA (g/g), different temperature reaction ( $^{\circ}\text{C}$ ) and different time reaction (h) using D-Optimal design. Factors (variables) such as ratio OL/HYOOA (w/w,  $X_1$ ), SA/HYOOA (w/w,  $X_2$ ), reaction temperature ( $^{\circ}\text{C}$ ,  $X_3$ ) and reaction time (h,  $X_4$ ) were performed under the same experimental conditions. The reactions were performed in a 250-mL three-necked flask equipped with a reflux condenser, and a contact thermometer. The reaction mixture was heated on a magnetic heater and stirrer until it reached the experiment temperature; catalyst SA and desiccant of silica gel (SG) were added to the mixture at that moment. The reaction temperatures were held constant within a range of  $\pm 1^{\circ}\text{C}$ . Mixture of HYOOA (5 g), OL (1-2 g) in 250-mL three-neck flask equipped with a cooler, dropping funnel and thermometer was heated for 1 h at  $90^{\circ}\text{C}$ , during the 1h reaction SG was put in the oven at  $180^{\circ}\text{C}$  for drying. After 1 h SG drying the SG (50% of the HYOOA) and SA (0.20-0.25 g) were added to the mixture. The reaction mixture was subsequently heated to different temperatures  $90$ – $110^{\circ}\text{C}$  and refluxed at different times 5-7 h at this temperature range. After reaction termination, the heating was stopped and the mixture was left to stand overnight at ambient temperature. After the reaction under conditions selected as optimal, the flask was allowed to cool to room temperature. The mixture was filtered using acetic acid (AA) as solvent to remove the SG from the product. The mixture was washed repeatedly with distilled water until all the catalyst was removed. The mixture was washed with the water and the organic layer was dried over magnesium sulfate and the solvent was removed using the vacuum evaporator. Excess OL in the mixture was removed using distillation method. The yield% of the ester product was determined. The FTIR and  $^{13}\text{C}$ ,  $^1\text{H}$  NMR were analyzed and the physicochemical properties of the product were also studied.

TABLE I  
INDEPENDENT VARIABLES AND THEIR LEVELS FOR D-OPTIMAL DESIGN OF THE ESTERIFICATION REACTION

Independent variables		Variable Levels		
		-1	0	+1
1. OL/HYOOA (g/g)	$X_1$	1.0	1.5	2.0
2. SA/HYOOA (g/g)	$X_2$	0.15	0.20	0.25
3. Temperature ( $^{\circ}\text{C}$ )	$X_3$	90	100	110
4. Time (h)	$X_4$	5	6	7

FTIR spectra were recorded neat on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI) with a Smart ARK accessory containing a 45 Ze Se trough in a scanning range of  $650$ – $4000\text{ cm}^{-1}$  for 32 scans at a spectral resolution of  $4\text{ cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a JEOL JNM-ECP 400 spectrometer operating at a frequency of 400.13 and

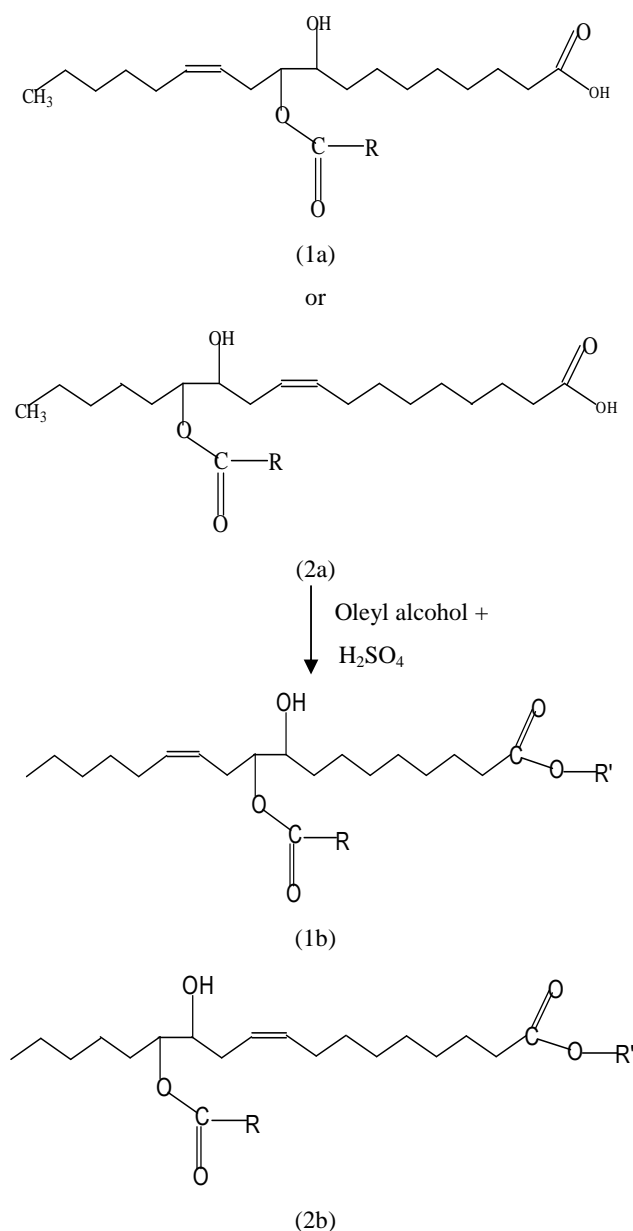


Fig. 1 Esterification of HYOOA.

Notes: 9-hydroxy-10-oleioxy-12-octadecanoic acid (1a); 12-hydroxy-13-oleioxy-9-octadecanoic acid (2a); oleyl 9-hydroxy-10-oleioxy-12-octadecanoate (1b); oleyl 12-hydroxy-13-oleioxy-9-octadecanoate (2b); oleic acid (R) and oleyl alcohol ( $\text{R}'$ ).

100.77 MHz, respectively, using a 5-mm broadband inverse Z-gradient probe in DMSO-d<sub>6</sub> (Cambridge Isotope Laboratories, Andover, MA) as solvent. Each spectrum was Fourier-transformed, phase-corrected, and integrated using MestRe-C 2.3a (Magnetic Resonance Companion, Santiago de Compostela, Spain) software.

### B. Experimental Design and Statistical Analysis

To explore the effect of the operation variables on the response in the region of investigation, a D-optimal design was performed. Ratio of OL/HYOOA (w/w,  $X_1$ ), ratio of SA/HYOOA (g,  $X_2$ ), reaction temperature (°C,  $X_3$ ) and reaction time (h,  $X_4$ ) were selected as independent variables. The range of values and coded levels of the variables are given in Table I.

A polynomial equation was used to predict the response as a function of independent variables and their interactions. In this work, the number of independent variables was three and therefore the response for the quadratic polynomials becomes:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} x_i x_j \quad (1)$$

Where  $\beta_0$ ;  $\beta_i$ ;  $\beta_{ii}$  and  $\beta_{ij}$  are constant, linear, square and interaction regression coefficient terms, respectively, and  $x_i$  and  $x_j$  are independent variables. The Minitab software version 14 (Minitab Inc., USA) was used for multiple regression analysis, analysis of variance (ANOVA), and analysis of ridge maximum of data in the response surface regression (RSREG) procedure. The goodness of fit of the model was evaluated by the coefficient of determination  $R^2$  and its statistical significance that was checked by the  $F$ -test.

## III. RESULTS AND DISCUSSION

Biolubricant oleyl 9(12)-Hydroxy-10(13)-oleioxy-12(9)-octadecanoate (OLHYOOT) was synthesized from direct esterification of HYOOA, where the corresponding HYOOA react with OL in the presence of a suitable catalyst. The acid catalysts are the most common catalyst used in biolubricant industry because the process proves faster and the reaction conditions are moderate compared to the alkali catalyst [13].

In the present study, biolubricant production using homogeneous acid-catalyzed esterification process sulfuric acid (SA) was proposed. The influence of the ratio of OL to HYOOA,  $X_1$  (1:1-2:1 w/w), ratio of SA to HYOOA,  $X_2$  (0.15:1-0.25:1 g/g), temperature reaction,  $X_3$  (90-110 °C), and reaction time,  $X_4$  (5-7 h) to the reaction was studied Table II. These four conditions were studied using design of experiment based on four variables (D-optimal design). The process variables were optimized using the Response Surface Methodology (RSM) in obtaining the maximum yield of biolubricant  $Y$ . This method was also applied to determine the significance and interaction of the variables affecting the biolubricant production.

Results obtained from the observed experiments are summarized in Table II. The results developed a second order

polynomial equation (in coded units) that could relate diesters biolubricant yield to the parameters study. The following quadratic model was explained in equation 2.

$$Y = +47.76 - 1.06X_1 - 5.60X_2 + 2.77X_3 + 9.31X_4 + 11.46X_1^2 - 4.90X_2^2 + 2.61X_3^2 + 5.95X_4^2 + 4.37X_1X_2 + 3.94X_1X_3 + 3.51X_1X_4 + 1.14X_2X_3 + 0.011X_2X_4 + 9.86X_3X_4 \quad (2)$$

Table II illustrates the yield% effect related with alcohol, catalyst, temperature and reaction time. As expected, at high temperature (110 °C) and higher in time (7 h) the yield% was higher 88.7% compared with temperatures of 90 and 100 °C. As described in the mechanism, most of the carboxylic acid groups were consequently converted into and ester bonds in the molecule. The decreasing of biolubricant yield% at a higher reaction temperature and higher time was probably as a result of losing of OL due to it did not condense effectively at a higher temperature as boiling point of OL is 107 °C [14].

TABLE II  
D-OPTIMAL DESIGN ARRANGEMENT AND YIELD% RESPONSE FOR OLHYOOT

Run no.	OL <sup>a</sup> /HYOOA <sup>b</sup> ( $X_1$ )	SA <sup>c</sup> /HYOOA ( $X_2$ )	Temp. <sup>d</sup> ( $X_3$ )	Time <sup>e</sup> ( $X_4$ )	Yield% <sup>f</sup> ( $Y$ )
1	1.00	0.15	90	7	78.3
2	1.50	0.20	100	7	66.7
3	1.50	0.15	100	6	38.7
4	1.00	0.20	100	6	45.7
5	1.00	0.25	110	5	41.5
6	2.00	0.25	90	5	43.1
7	2.00	0.20	90	7	47.5
8	2.00	0.25	110	7	84.4
9	1.00	0.25	90	7	45.9
10	2.00	0.25	90	5	50.1
11	1.00	0.20	110	7	88.7
12	2.00	0.20	110	5	46.4
13	1.50	0.15	110	7	75.9
14	2.00	0.15	90	5	60.2
15	1.50	0.23	105	5.5	44.5
16	1.50	0.20	90	6	51.5
17	2.00	0.15	90	7	58.1
18	2.00	0.25	90	7	68.2
19	1.00	0.20	90	5	78.3
20	1.00	0.15	110	5	55.7
21	2.00	0.15	100	7	76.7
22	2.00	0.15	110	6	65.9
23	1.00	0.25	110	7	69.5
24	2.00	0.15	90	5	50.8
25	2.00	0.20	100	6	72.3

Notes: oleyl alcohol, g (a); 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoic acid (HYOOA), g (b); sulfuric acid, g (c); temperature reaction, °C (d); reaction time, h (e); yield% of oleyl 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate (OLHYOOT) (f).

TABLE III

REGRESSION COEFFICIENTS OF THE PREDICTED QUADRATIC POLYNOMIAL MODEL FOR RESPONSE VARIABLES OF THE YIELD% OF OLHYOOT

Variables	Coefficients ( $\beta$ ), yield% of OLHYOOT ( $Y$ )	$T$	$P$	Notability
Intercept	47.76	2.35	0.0890	
Linear				
$X_1$	-1.06	0.15	0.7078	
$X_2$	-5.60	3.39	0.0955	
$X_3$	2.77	1.02	0.3365	
$X_4$	9.31	11.21	0.0074	***
Quadratic				
$X_{11}$	11.46	3.03	0.1124	
$X_{22}$	-4.90	0.84	0.3816	
$X_{33}$	2.61	0.14	0.7156	
$X_{44}$	5.95	0.68	0.4288	
Interaction				
$X_{12}$	4.37	1.65	0.2279	
$X_{13}$	3.94	1.68	0.2237	
$X_{14}$	3.51	1.34	0.2740	
$X_{23}$	1.14	0.12	0.7364	
$X_{24}$	0.011	1.234E-005	0.9973	
$X_{34}$	9.86	10.54	0.0088	***
$R^2$	0.76			

Notes:  $X_1$ = OL/HYOOA;  $X_2$ = SA/HYOOA;  $X_3$ = reaction temperature;  $X_4$ = reaction time\*\*  $P < 0.05$ ; \*\*\*  $P < 0.01$ .  $T$ :  $F$  test value

See Table II for a description of the abbreviations

The quadratic regression coefficient obtained by employing a least squares method technique to predict quadratic polynomial models for the yield% ( $Y$ ) of OLHYOOT are given in Table III. The yield% of OLHYOOT ( $Y$ ), the linear term of reaction time ( $X_4$ ) and interaction terms of reaction temperature and reaction time ( $X_{34}$ ) were high significant ( $p < 0.01$ ).

The lack of fit  $F$ -value for the  $Y$  response showed that the lack of fit is not significant ( $p > 0.05$ ) relative to the pure error. This indicates that all the models predicted for the  $Y$  response were adequate. Regression models for data on response  $Y$  was significant ( $p < 0.05$ ) with satisfactory  $R^2$ . However, the predicted values match the observed values reasonably well, with  $R^2$  of 0.76, and the model was significant. Table IV summarizes the analysis of variance (ANOVA) of all the responses of this study.

RSM is one of the best ways of evaluating the relationships between responses, variables and interactions that exist. Significant interaction variables in the fitted models Table (3) were chosen as the axes (ratio of OL/HYOOA;  $X_1$ , ratio of SA/HYOOA;  $X_2$  reaction temperature;  $X_3$  and reaction time  $X_4$ ) for the response surface plots. The relationships between independent and dependent variables are shown in the three-dimensional representation as response surfaces. In a contour plot, curves of equal response values are drawn on a plane whose coordinates represent the levels of the independent factors. Each contour represents a specific value for the height of the surface above the plane defined for combination of the levels of the factors. Therefore, different surface height values

enable one to focus attention on the levels of the factors at which changes in the surface height occur [15].

TABLE IV

ANALYSIS OF VARIANCE, SHOWING THE EFFECT OF THE VARIABLES AS LINEAR, SQUARE AND INTERACTIONS ON THE RESPONSE  $Y$  (YIELD% OF OLHYOOT) OF THE D-OPTIMAL DESIGN

Source	$Df$	Sum of squares	Mean square	$F$ value	$P$
Mean	1	90552.85	90552.85		
Linear	4	1680.18	420.04	2.29	0.0956
2FI	6	1577.15	262.86	1.76	0.1803
Quadratic	4	847.96	211.99	1.70	0.2257
Lack-of-fit	8	1177.54	147.19	4.29	0.2029
Pure error	2	68.68	34.34		
Total	25	1.136E+005	3836.17		

Canonical analysis was performed on the predicted quadratic polynomial models to examine the overall shape of the response surface curves and used to characterize the nature of the stationary points. Canonical analysis is a mathematical approach used to locate the stationary point of the response surface and to determine whether it represents a maximum, minimum or saddle point [15].

Fig. 2 is the Design-Expert plots for all the responses. In the diesters biolubricant reaction of OLHYOOT, performing the technique using high reaction temperature and high time would give the desired yield% of OLHYOOT as shown in Fig. 2. The biolubricant yield% increased as the reaction time increased to its high level (7 h). The biolubricant yield% also

increased with reaction temperature to its central level (110 °C), and the stronger influence of reaction time occurred when reaction time was at its high level. The relationships between the parameters and yield% of OLHYOOT were linear or almost linear Fig. 2.

Optimum conditions of the experiment to obtain high yield% of OLHYOOT were predicted at ratio of OL/HYOOA of 1:1 g/g, catalyst SA of 0.20:1 g/g, reaction temperature 110 °C and 4.5 h of reaction time. At this condition, the Yield% of OLHYOOT was 88.7. The observed value was reasonably close to the predicted value as shown in Fig. 3. Experimental variables should be carefully controlled in order to obtain reasonable yield.

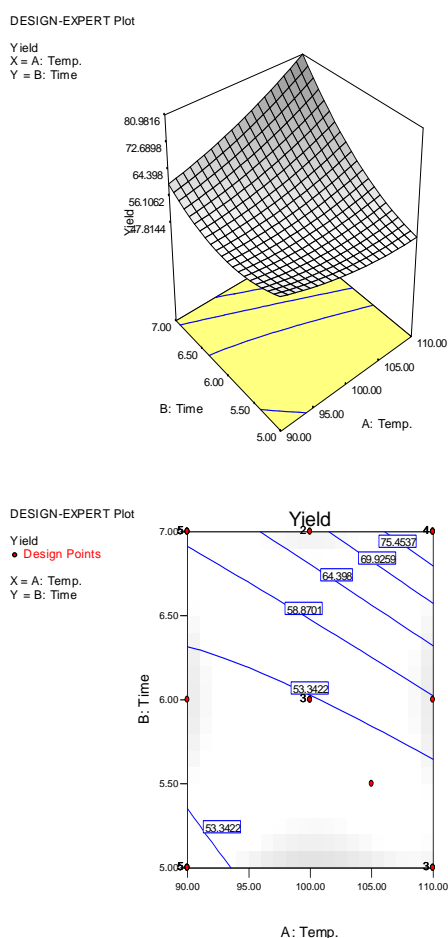


Fig. 2 Response surface (a) and contour plots (b) for the effect of the ratio of OL/HYOOA (w/w,  $X_1$ ) and ratio of SA/HYOOA ( $X_2$ , g) on the yield% of OLHYOOT.

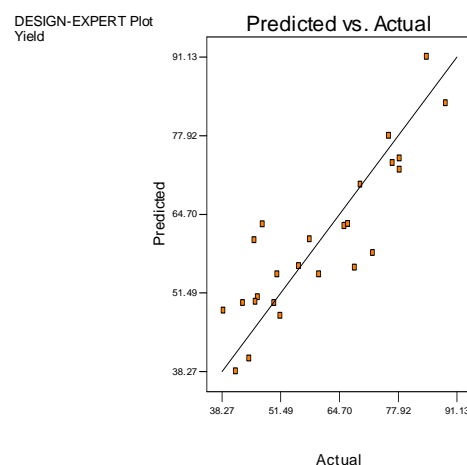


Fig. 3 Predicted vs. actual plot of Y (OLHYOOT)

The spectrum from the FTIR analysis displays several absorption peaks as shown in Fig. 4. The main peaks and their assignment to functional groups are given in Table V. FTIR peaks of OLHYOOT indicated disappearance of absorption band at  $1711\text{ cm}^{-1}$  which belong to the C=O carboxylic acid, while appear in HYOOA. For the ester carbonyl functional groups C=O at  $1737\text{ cm}^{-1}$  of OLHYOOT which showed the same absorption band in HYOOA at  $1738\text{ cm}^{-1}$ . FTIR Peaks at  $2925$  to  $2855\text{ cm}^{-1}$  indicated the  $\text{CH}_2$  and  $\text{CH}_3$  scissoring of HYOOA and OLHYOOT. The FTIR spectroscopy analysis of HYOOA and OLHYOOT indicated the presence of peak at  $3003\text{ cm}^{-1}$  which belong to the double bond C=C (stretching aliphatic) while at  $3445$  and  $3413\text{ cm}^{-1}$  belong to -OH stretching of OLHYOOT and HYOOA, respectively [13].

TABLE V  
THE MAIN WAVELENGTHS IN FTIR FUNCTIONAL GROUPS OF HYOOA AND OLHYOOT

Wavelength of HYOOA <sup>a</sup>	Wavelength of OLHYOOT <sup>b</sup>	Functional groups
3413	3445	OH stretching (alcohol)
3003	3003	C=C bending vibration (aliphatic)
2925, 2855	2925, 2554	C-H stretching vibration (aliphatic)
1737	1738	C=O stretching vibration (ester)
1711	-	C=O stretching vibration (carboxylic)
1461	1461	C-H scissoring for methylene
1176, 1117	1173, 1117	C-O stretching vibration (ester)
1279	-	C-O stretching asymmetric (carboxylic)
967	967	C-H bending vibration (alkene)
723	723	C-H group vibration (aliphatic)

Notes: 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoic acid (a); oleyl 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate (b)

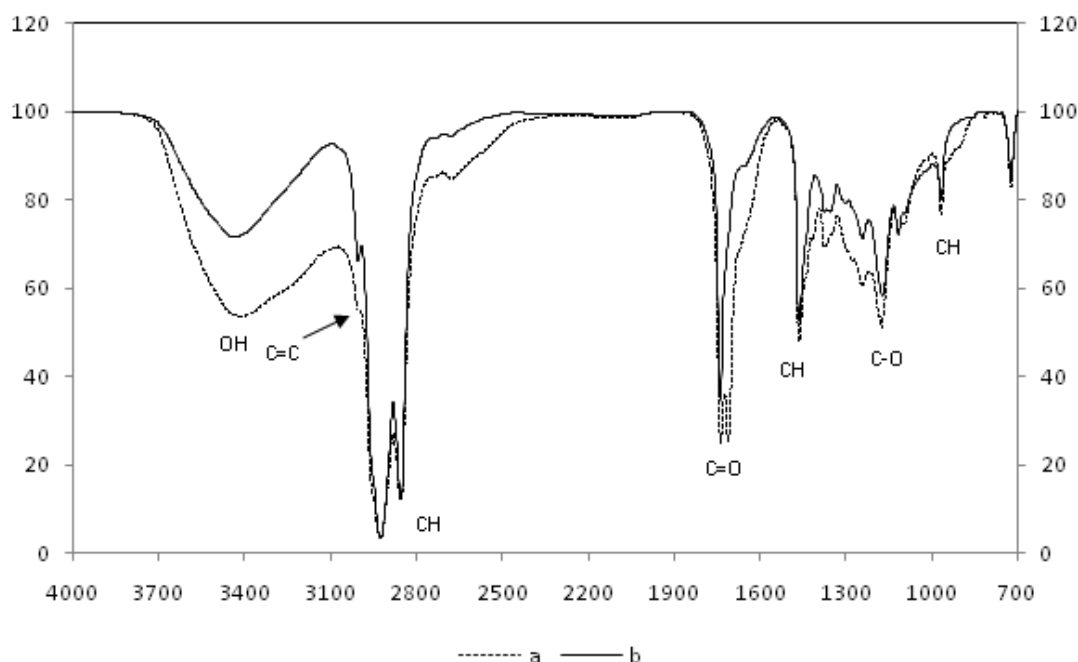


Fig. 4 FTIR spectrum of the HYOOA (a) and OLHYOOT (b)

The peaks at 1176, 1173 and 1117  $\text{cm}^{-1}$  of OLHYOOT and HYOOA referred to as C-O stretching ester. FTIR spectrum also showed absorption bands at 723  $\text{cm}^{-1}$  of C-H group vibration. A similar observation has been reported for the FTIR spectrum of other studies [13].

$^{13}\text{C}$  NMR spectroscopy being one of the less naturally-abundant isotopes of carbon also exhibits the phenomenon but until comparatively recent development in instrumentation and data processing have been made,  $^{13}\text{C}$  NMR spectroscopy is now much more accessible and since all carbon atoms in the organic compounds give distinctive signals, whether or not they are linked to protons, a great deal of structural information can be obtained from the spectra.

Fig. 5 (a) and (b) indicates the  $^{13}\text{C}$  NMR spectrum of HYOOA and OLHYOOT, respectively. The  $^{13}\text{C}$  spectroscopy shows the main signals assignment of HYOOA and OLHYOOT as shown in Table VI. The Fig. 5 (b) showed disappearance of carbon atom of the carbonyl group (carboxylic acid) of OLHYOOT which has appeared for HYOOA at 178.11 ppm while at 173.93-174.01 ppm have appeared in OLHYOOT and HYOOA which refer to ester group. The signals at 127.90 to 130.74 ppm refer to the unsaturated carbon atoms (olefinic carbons) for both HYOOA and OLHYOOT.

Fig. 5 (b) can be confirmed appearance OH alcohol of OLHYOOT and HYOOA at about 64.37 and 64.41 ppm, respectively. The other distinctive signals were aliphatic carbons for OLHYOOT and HYOOA at about 25.76-34.38

ppm and, which are common for these types of compounds which belong to the methylene carbon atoms of MEOA and HYOOA [13].

TABLE VI  
THE MAIN SIGNALS PRESENT IN  $^{13}\text{C}$  NMR FUNCTIONAL GROUPS OF HYOOA AND OLHYOOT

$\delta$ (ppm) of HYOOA <sup>a</sup>	$\delta$ (ppm) of OLHYOOT <sup>b</sup>	Assignment
25.76-34.38	25.75-34.37	Aliphatic Carbons
64.41	64.37	Alcohol
127.90-130.57	129.61-130.46	Olefinic carbons
174.01	173.93	Ester
178.11	-	Carboxylic acid

Notes: 9,12-hydroxy-10,13-oleioxy-12,9-octadecanoic acid (a) ; 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate (b).

$^1\text{H}$  NMR Proton magnetic resonance spectroscopy is the most valuable form of the technique for lipid analysis. The frequency at which any given hydrogen atom in an organic compound resonates is strongly dependent on its precise molecular environment. The  $^1\text{H}$  NMR spectroscopy shows the main signals assignments in HYOOA and OLHYOOT as shown in Table VII. Fig. 6. The distinguishable peaks appeared in OLHYOOT and HYOOA for -CH-OH at 3.62 ppm while -CHOCOR at 4.06 and 4.05 ppm, respectively Fig. 6 (a) and (b).

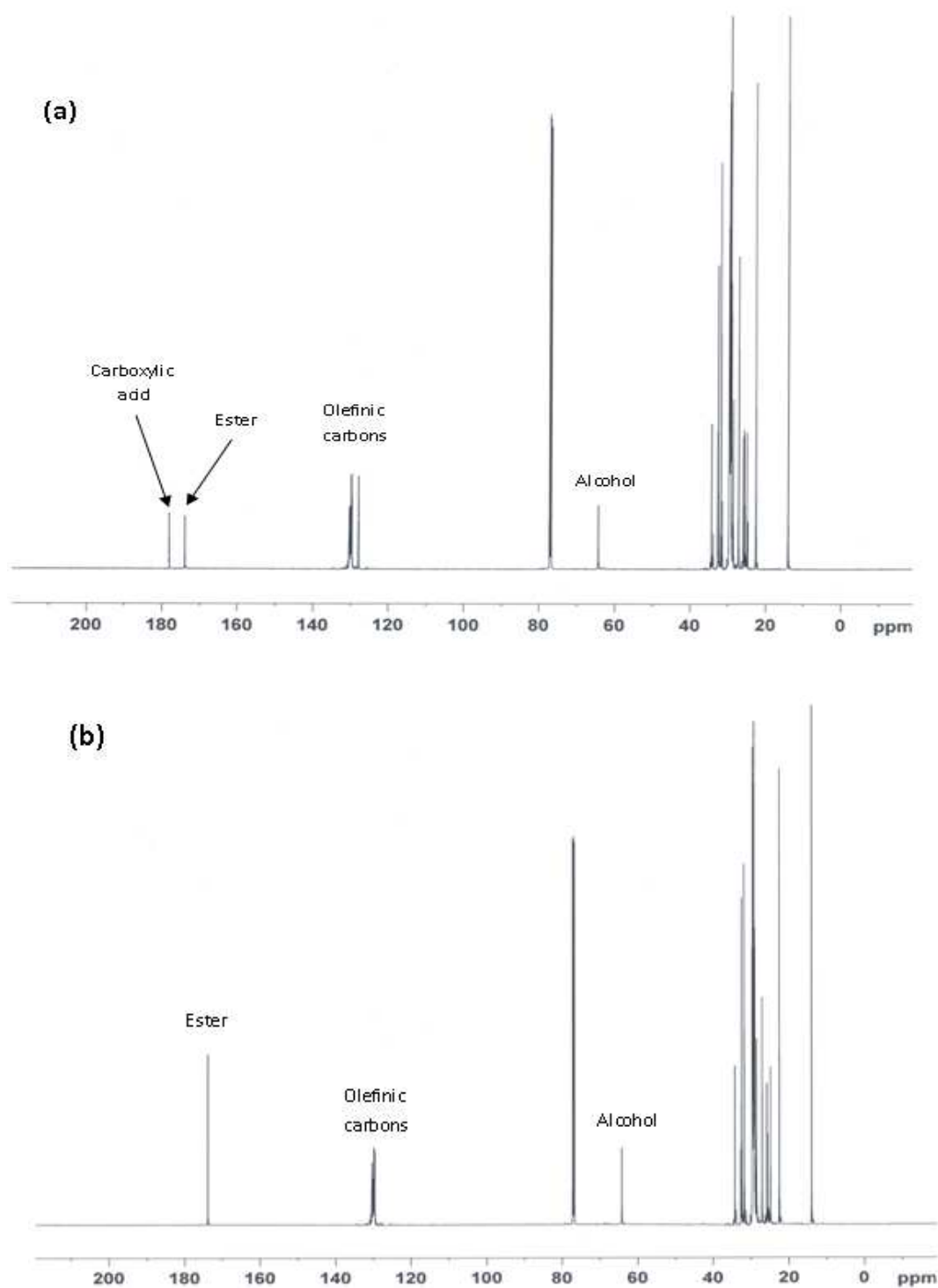


Fig. 5  $^{13}\text{C}$  NMR spectrum of HYOOA (a) and OLHYOOT (b)

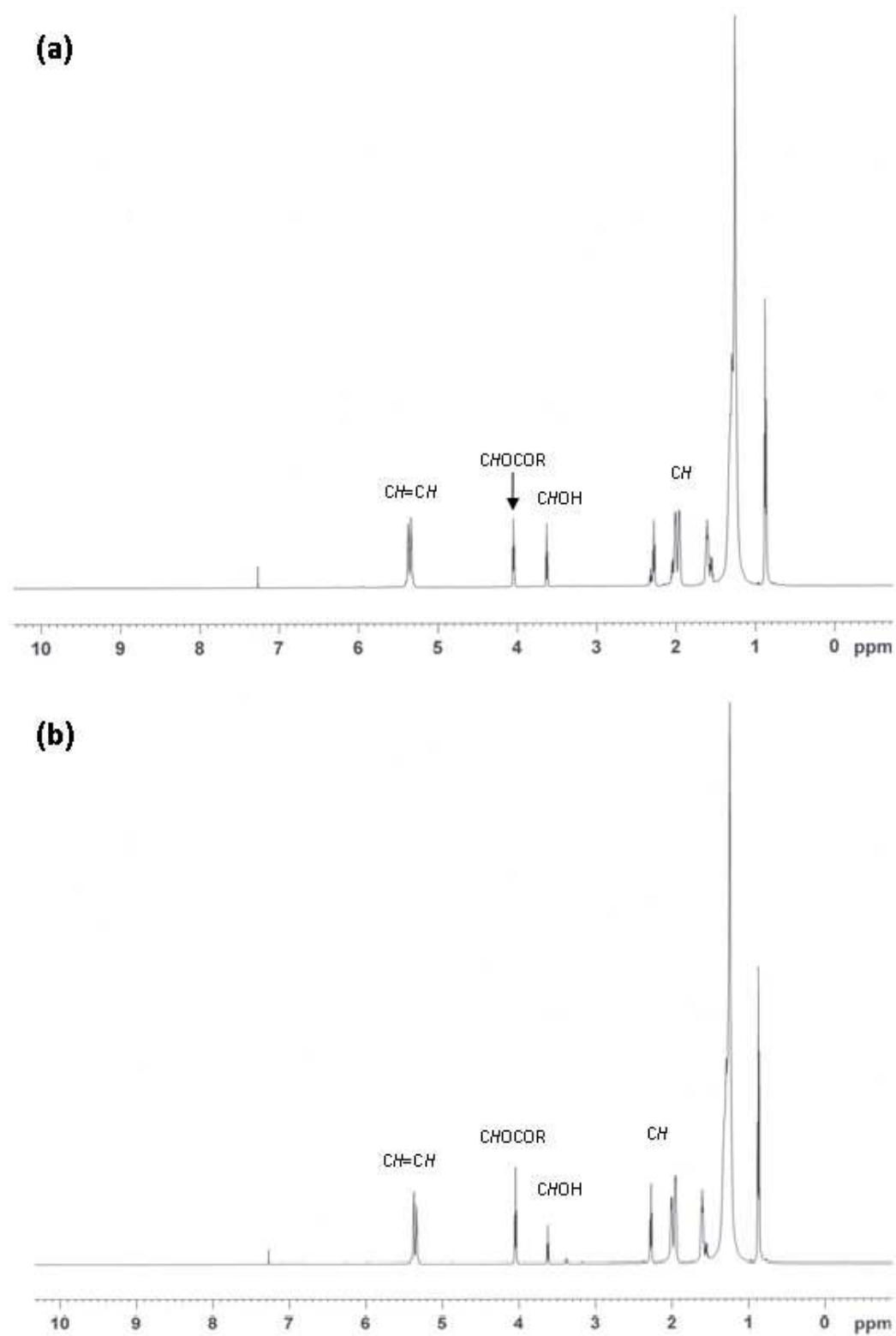


Fig. 6  $^1\text{H}$  NMR spectrum of HYOOA (a) and OLHYOOT (b)



TABLE VII  
THE MAIN SIGNALS PRESENT IN <sup>1</sup>H NMR FUNCTIONAL GROUPS OF HYOOA  
AND OLHYOOT

$\delta$ (ppm) of HYOOA <sup>a</sup>	$\delta$ (ppm) of OLHYOOT <sup>b</sup>	Assignment
0.82-0.84	0.86-0.88	-CH <sub>3</sub>
1.23-2.06	1.25-2.01	-CH <sub>2</sub>
2.26-2.33	2.26-2.29	-CH
3.62	3.62	-CHOH
4.06	4.05	-CHOCOR
5.31-5.40	5.33-5.37	-CH=CH-

Notes: 9,12-hydroxy-10,13-oleioxy-12,9-octadecanoic acid (a) ; 9(12)-hydroxy-10(13)-oleioxy-12(9)-octadecanoate (b).

The signals at 0.82-0.88 ppm referred to the methylene group (-CH<sub>3</sub>) of OLHYOOT which also appear in HYOOA next to the terminal methyl (-CH<sub>2</sub>) at 1.23-2.06 ppm of OLHYOOT and HYOOA. The other distinctive signals were methine at about 2.26-2.33 ppm, which are common for these types of compounds [16]. However, the methane proton signals (-CH=CH-) was shifted upfield at about 5.33-5.37 ppm of OLHYOOT [13].

#### IV. CONCLUSION

The process describes a systematic approach to modify HYOOA to yield biolubricant basestocks 9(12)-Hydroxy-10(13)-oleioxy-12(9)-octadecanoate (OLHYOOT). Based on the results obtained under some conditions, hydroxy ester products obtain high yield% of OLHYOOT were predicted at ratio of OL/HYOOA of 1:1 g/g, catalyst SA of 0.20:1 g/g, reaction temperature 110 °C and 4.5 h of reaction time.

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