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Biolubricant Production from Palm Stearin Fatty Acids and Pentaerythritol[†]

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Palm stearin was converted to biolubricant through the chemical modification process. Saturated palm stearin fatty acids (SPSFA) and unsaturated palm stearin fatty acids (UPSFA) were reacted with pentaerythritol (PE) *via* Fischer esterification to produce SPE-ester and UPE-ester. Both esters were successfully synthesized in a three-necked round bottom flask based on four parameters, and these were reaction temperature, reaction time, sulphuric acid (H_2SO_4) concentration as a catalyst and the molar ratio of reactants fixed to 5:1 for both SPSFA:PE and UPSFA:PE. About 69% of SPE-esters and 61% of UPE-esters were produced. Products characterization was performed by Fourier transformation infrared spectroscopy, proton, and carbon nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectroscopy analysis techniques. The presence of ester carboxyl band, v(C=O) was at 1742 cm^{-1} for both SPE-ester and UPE-ester. SPE-ester and UPE-ester recorded their pour point at 44ºC and 9ºC, the flash point at 243ºC (SPE-ester) and 232ºC (UPE-esters), viscosity index about 140 (SPE-ester) and 151 (UPE-ester), oxidative stability at 269ºC for SPE-ester and 238ºC for UPE-ester. SPE-ester and UPE-ester could be categorized as *ISO VG 46* and *ISO VG 100* grade lubricant, respectively.

Key words: Palm stearin; Fischer esterification; pentaerythritol; biolubricant; renewable sources

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Vegetable-based oils are showing great potential and excellent feedstock to replace the conventional mineral oils for lubricant production. They are structurally similar to the long chained hydrocarbons in mineral oils with the characteristics of being renewable, non-toxic, economical and environmentally friendly. Therefore, biolubricant products have been extensively explored. Right lubricants have been explored since the development of petroleum-based oil in the 1800s [1]. Science and technology have made remarkable improvements in the properties and performances of the petroleum-based lubricant. Lubricants are highly used in variety of applications. Due to the fact, there are high demands of these non-renewable sources of oil. To overcome this, researchers have found a solution to the alternative of petroleum-based oil that meeting massive insufficiency sources in the near future. Few countries such as the United States and Europe began to show interest in proving the ability of the renewable sources focusing on plant-based oil to be chemically altered [2] to have the similar basic structure of petroleum-based lubricant [1]. As reported, sunflower [3], safflower [3], soybean [3], cottonseed [3], rapeseed [3], peanut [3], jatropha [4] and palm oil [5] are considered as potential alternatives to the petroleum-based oil [6].

Improvements have been made and proven that the biolubricants own better properties and performance than that of the petroleum-based lubricant. According to Zulkifli *et al*. (2013) [7], biolubricant posses high flash point, high viscosity index, high lubricity and low evaporative loss. It is also non-toxic, biodegradable [8] and well agreed by Abdul *et al*. (2011) [9] that biolubricant is less expensive. Over the decades, biolubricant has been studied throughout the world. Malaysia is among the largest exporter of palm oil in the world. The liquid fraction of palm oil was reported to be highly potential in biolubricant production such as palm oil mill effluent, (POME) [5, 10] and palm olein (PO) [11, 12]. However, there is a limited study on solid fraction as biolubricant feedstock such as palm stearin (PS). Some studies have been done before in utilizing PS as biolubricant feedstock. One of the research done by using chemical modification with polyhydric alcohol [13]. Palm stearin is a solid fraction obtained by the fractionation of palm oil after crystallization at controlled temperatures. It can be considered as a low-cost by-product in palm olein production [14]. It is composed of about 50 to 68% of saturated fatty acid which is palmitic acid (C16:0). While there is only 20 to 34% of unsaturated fatty acid—oleic acid (C18:1) [15]. This causes the iodine

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value of PS to be low due to the high content of saturated triacylglycerol (TAG). PS can be utilized as a potential feedstock in biolubricant production by separating and purifying the unsaturated fatty acids from saturated fatty acids.

The characteristics and the composition of fatty acids in palm stearin are suitable as an alternative source for biolubricant production. Saturated and unsaturated fatty acids were utilized in various medical applications like drug delivery and temporary implantable devices. Fatty acids based polymer possess few properties such as low melting point, fluid enough for easy injection, flexible before and during degradation, easy manufacture and reasonable cost to claim their utility as drug delivery carriers [16]. For the food industry, unsaturated and saturated fatty acids will be utilized as feedstock in margarine and shortening production. Vegetable oils such as soybean oil, canola oil, rapeseed oil, and palm oil have lubricity properties. However, the original triacylglycerol structure introduced some problems with oxidative stability property. The poor oxidative stability is due to the presence of beta-hydrogen attached to the carbon of glycerol backbone [17]. Thus, pentaeryhtritol (PE) was added to replace glycerol for the chemical modifications to improve the oxidative stability, lubricity, and fire resistance. This is due to the symmetrical structure of PE. Fatty acid route synthesis is one of the promising reaction pathway rather than TAG route to improve the oxidative stability of biolubricant products. Chauhan and Chhibber (2013) [2] reported that saturated fatty acids (SFA) resulted in a better thermo oxidative stability and weak pour point due to the linear structure of acid. Unsaturated fatty acids (UFA) have a lower pour point and weak resistant to oxidation at high temperature [13].

The production of biolubricant is a process which involves the experimental process such as reaction time, temperature, catalyst used and ratio of SPSFA/UPSFA: PE. A series of an experiment is carried out towards one conclusion. Biolubricant to be produced needs to be a quality product in a large quantity with the least production cost. The classic optimization method incurred plenty of time. Recently, one method has found which works on the principle of statistics and mathematics that can optimize the process parameter in a concise time. It is a mathematical modeling called response surface methodology (RSM). It is a scientific method which require observed and gathered data regarding the working of process and system works with less use of chemicals, laboratory equipment and setups, human resources and saves valuable time [18] to generate sufficient information for statistically acceptable results [19] with fewer experimental runs.

In this paper, the synthesis of biolubricant from SPSFA and UPSFA *via* Fischer esterification with PE was reported. The optimization was performed using RSM with D-optimal design. A sequence of the experimental procedure was conducted to determine the optimum conditions, temperature, reaction time, catalyst and SPSFA/UPSFA, PE ratio for the production of SPE-esters and UPE-esters. Synthesized esters were characterized for their lubrication properties.

MATERIALS AND METHODS

Materials

Refined, bleached and deodorised (RBDPS) were obtained from Jomalina Refinery, Sime Darby Plantation Sdn. Bhd. RBDPS was prepared for Sime Darby Research Sdn, Bhd. All chemicals purchased from Systerm and R&M Chemicals. Palm stearin fatty acid (PSFA) was prepared *via* hydrolysis (lab scale) in Universiti Kebangsaan Malaysia.

Separation of SPSFA and UPSFA

The separation of palm stearin fatty acids into SPSFA and UPSFA is based on a method reported by Arnold (1926) with a slight modification in the method. A series of optimization was carried out whereby the methanol was used to dissolve and PSFA with the ratio of PSFA: methanol; 1:9 and stored at -20°C for 24 hours. After 24 hours, two layers were formed where the underlying layer was SPSFA which is a white solid and yellow liquid at the top which is a mixture of UPSFA, and methanol. The frozen mixture was filtered with borosilicate glass filter funnel (porosity 2) connected to a vacuum pump to speed up the filtration uniformly. The solid SPSFA (top) were rinsed using cold methanol to dissolve the remaining unsaturated fatty acids (UFA). The entire process was repeated 3 times by dissolving the SPSFA (top) and UPSFA (bottom) in methanol until the separation result was completely ensured for use in the next process. The unsaturated fatty acid was separated from methanol by using the rotary evaporator. Both SPSFA and UPSFA were dried in a vacuum oven at 45°C for 24 hours.

Response Surface Methodology

An experimental design used for the series of parameters for SPE-esters and UPE-esters synthesis by esterification of SPSFA and UPSFA with PE respectively was built by RSM with the Design Expert Version 6.0.10. D-optimal design factorial model was used in this study to optimize the dependent variables in solid fractions esterification reaction conducted with 18 experimental runs. The selection of range for the independent variables was based on the experimental studies conducted in the lab in a fully randomized order. The experimental design for the esterification process according to parameters is given in Table 1 to produce SPE-esters, and Table 2 for the production of UPE-esters.

The independent variables chosen were temperature (A_1, A_2), reaction time (B_1, B_2) and catalyst (C_1, C_2). Percentage of tetraesters conversion (Y) of SPE-esters (Y_1) and UPE-esters (Y_2) were chosen to be the target of the response parameter as a dependent variable. The significance of the model was determined by the statistical parameter. Model graphs were plotted resulting from the equation, using the same software.

Table 1. Parameters for esterification of SPSFA and PE.

Run	A_1, temperature (ºC)	B_1, reaction time (hours)	C_1, catalyst (%)	D_1, molar ratio (SPSFA:PE)
1	170	3	1	5:1
2	170	3	3	5:1
3	170	4	1	5:1
4	170	6	2	5:1
5	200	3	3	5:1
6	190	5	2.5	5:1
7	180	5	1	5:1
8	170	6	1	5:1
9	200	6	3	5:1
10	200	1	1	5:1
11	200	1	1	5:1
12	200	1	2	5:1
13	200	2	3	5:1
14	170	3	3	5:1
15	190	2	2	5:1
16	170	3	3	5:1
17	200	1	1	5:1
18	170	6	3	5:1

Table 2. Parameters for esterification of UPSFA and PE.

Run	A_2, temperature (ºC)	B_2, reaction time (hours)	C_2, catalyst (%)	D_2, molar ratio (SPSFA:PE)
1	170	6	1	5:1
2	170	3	1	5:1
3	170	4	2	5:1
4	200	6	1	5:1
5	200	3	1	5:1
6	170	3	3	5:1
7	170	6	1	5:1
8	170	3	3	5:1
9	190	5	2.5	5:1
10	200	4	3	5:1
11	180	4	2	5:1
12	170	6	3	5:1
13	200	6	3	5:1
14	200	6	1	5:1
15	190	3	2	5:1
16	170	3	1	5:1
17	200	3	3	5:1
18	200	3	1	5:1

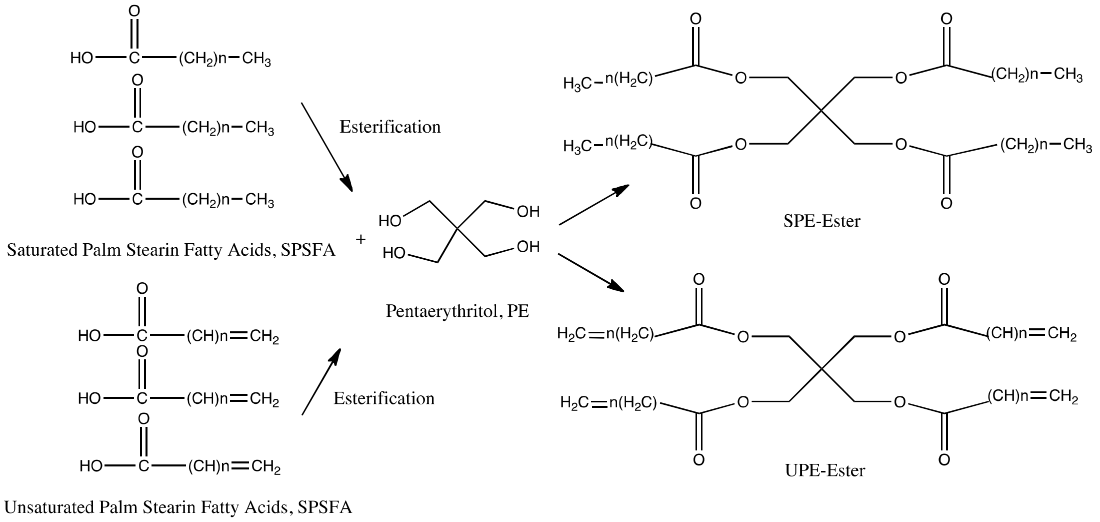


Figure 1. Synthesis pathway of SPE-ester and UPE-ester.

Synthesis of SPE-ester and UPE-ester

Saturated and unsaturated palm stearin fatty acids underwent esterification with pentaerythritol (PE) respectively under a condition with four parameters: temperature, reaction time, percent catalyst and molar ratio of SPSFA: PE (Table 1) and UPSFA: PE (Table 2). The temperature was set at the range of 170-210 °C for 5-6 hours. 1-3% catalyst was loaded and the molar ratio was 5:1. The esterification reaction was set up with reflux condenser by adding SPSFA/UPSFA to PE, sulphuric acid as a catalyst and 80 ml toluene into 250 ml three-necked round bottom flask equipped with a thermometer, magnetic stirrer and Dean-Stark apparatus. Dean-Stark was used to carry out the distillation of water-toluene. The water formed from the reaction was continuously removed. When the reaction was completed, the product was separated from the catalyst and unreacted fatty acids by adding sodium bicarbonate and sodium chloride solution into the separatory flask. The sample was separated from the washing solution by using ethyl acetate. The product was analysed by using Fourier transform infrared (FTIR) spectroscopy, gas chromatography (GC-FID) and NMR spectroscopy and its physicochemical properties. The esterification reaction for both SPSFA and UPSFA with PE are shown in Figure 1.

Characterization

The percentage composition of esters (SPE-esters and UPE-esters) was determined by using gas chromatography equipped with flame ionization detector (GC-FID). For the sample preparation, about 0.03±0.005 g sample was diluted in 1 ml ethyl acetate (GC grade). The GC-FID was equipped with DB-5ht capillary column (30m × 0.25 mm × 0.10 μm). The detector temperature was programmed at 400°C. Column temperature gradient ranged from 100 to 380°C at a flow rate of 5 min^{-1} and held for 20 minutes. Nitrogen was used as the carrier gas. The presences of the ester structure in esters were determined using FTIR spectroscopy. Esters were contacted with NaCl plate and scanned from 4000 to 650 cm^{-1}. The structures of esters were confirmed by the means of ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy at the frequency of 400 and 100.61 MHz, respectively. 570 µl of deuterated chloroform ($CDCl_3$) was added into the sample of esters for the analysis.

Physicochemical properties are pour point, flash point, fire point, viscosity index, and oxidative stability. Pour point is the lowest temperature at which movement of the specimen is observed. Pour point has traditionally been measured when the sample no longer moves on tilting the U-tube containing the sample [20]. Both esters pour point was measured by using standard method; *ASTM D 97-66* (Reapproved 1971).

Flash point is the minimum temperature at which the liquid produces enough vapour above it surface that able to form ignitable mixture with air [16]. The standard method *ASTM D92* was used to determine the flash point of both esters. It is important to note that the sample was run triplicate and the average value recorded.

Viscosity is a quantitative measure of its resistance to flow. Kinematic viscosity was measured at 40 and 100°C by using Anton Paar Physica MCR 301 Rheometer. The viscosity and viscosity index was measured using *ASTM D445-79*. Each sample was run triplicate and average value was recorded. It is an important property in the application of biolubricant [11].

The oxidative stability was measured using pressurized differential scanning calorimeter. In this work, the analysis was carried out using a programmable heating rate mode with a constant flow dry of O_2 inside the pressure chamber to determine the onset temperature and the signal maximum temperature (SMT). The SMT is the temperature at which maximum heat output is observed in the sample during the oxidative degradation.

RESULTS AND DISCUSSION

RBDPS contains ester, namely triglycerides (TAG) that had undergone chemical modification with PE. RBDPS were conducted under hydrolysis produce PSFA and separated into SPSFA and UPSFA for a further reaction; esterification with PE with the presence of sulphuric acid as catalyst. The esterification reaction was between SPSFA and UPSFA with PE to form SPE-ester and UPE-ester (Figure 1), respectively.

SPE-ester and UPE-ester were synthesized to form a branching structure biolubricant that have higher thermal stability compared to TAG structure in RBDPS [13]. On top of that, the presence of the tertiary β-H group in glyceride moeity resulted in low thermal and oxidative stability [12]. Thus, by removing the β-H by using PE will increase the thermal and oxidative stability. Presence of multiple C=C was widely reported to be prone to accelerating oxidative degradation, therefore the PSFA produced in this study consisted less C=C to reduce the oxidative degradation in biolubricant. Esterification reaction between SPSFA and UPSFA with PE was an approach to improve the properties of TAG in RBDPS.

Model Analysis

RSM evaluates interactions between responses and variables. The relationships between independent (temperature, time, catalyst and SPSFA and UPSFA ratio) and dependent (response) variables are shown in the three-dimensional representation as response surfaces. The response surfaces for the percentage of tetraester conversion were given in Figures 2(a) and 3(a). Both esters were designed experimentally by using D-optimal design (Tables 3 and 4) and the esters produced were analysed by using RSM. Based on the RSM analysis, the quadratic model of the conversion of tetraester is presented as Equation 1 for SPE-ester and Equation 2 for UPE-ester.

$$Y_1 = 50.38 + 2.06\mathrm{A}_1 - 2.78B_1 + 18.88C_1 - 11.36(A_1)^2 - 0.71(B_1)^2 + \mathrm{O}.76(C_1)^2 - 5.07A_1B_1 + 8.21A_1C - 12.04B_1C_1 \quad (1)$$

$$Y_2 = 48.76 + 12.97A_2 + 1.37B_2 + 0.82C_2 + 16.85(A_2)^2 - 25.55(B_2)^2 - 9.60(C_2)^2 - 2.03A_2B_2 - 2.24A_2\mathrm{C}_2 + 2.90B_2C_2 \quad (2)$$

Y_1 and Y_2 represent the conversion of tetraesters for SPE-ester and UPE-ester, respectively. A_1, A_2, B_1, B_2, C_1 and C_2 are the coded variables in the esterification reaction. The positive sign of the coeffiecient in linear term reveals that with an increasing the variables, the tetraesters conversion increases linearly, while negative sign indicates antagonistic effect. Equation (1) indicates that the catalyst loading has the strongest effect on the response since the coefficient of C_1 (18.88) is the largest compared to the other investigated factors. While Equation (2) indicates temperature has the most substantial effect on the response since the coefficient of A_2 (12.97) is the largest than that of the other investigated factors.

Statistical analysis includes the interaction effects and the main results of the variables on the conversion of tetraesters. The ANOVA tests the statistical significance of each effect by comparing with the mean square against the estimated experimental error with the range of experimental conditions. Statistical analysis of ANOVA of the main effects and the interactions for the response surface quadratic model are shown in Tables 3 and 4 for SPE-ester and UPE-ester, respectively.

Table 3. ANOVA for response surface quadratic model for SPE-esters.

Source	Sum of squares	DF	Mean square	F-value	Prob>F	
Model	8060.92	9	895.66	0.79	0.6376	Not significant
A	58.80	1	58.80	0.052	0.8259	
B	98.09	1	98.09	0.086	0.7765	
C	4361.26	1	4361.26	3.83	0.0859	
A^2	167.10	1	167.10	0.15	0.7115	
B^2	0.87	1	0.87	0.00762	0.9787	
C^2	1.20	1	1.20	0.00105	0.9749	
AB	288.45	1	288.45	0.25	0.6282	
AC	740.07	1	740.07	0.65	0.4433	
BC	1517.67	1	1517.67	1.33	0.2814	
Residual	9102.05	8	1137.76			
Lack of fit	2565.97	4	641.49	0.39	0.8064	Not significant
Pure error	6536.08	4	1634.02			
Cor. total	17162.97	17				

Table 4. ANOVA for response surface quadratic model for UPE-esters.

Source	Sum of squares	DF	Mean square	F-value	Prob>F	
Model	4369.28	9	485.54	0.57	0.7896	Not significant
A	2126.93	1	2126.93	2.50	0.1524	
B	21.64	1	21.64	0.025	0.8772	
C	8.58	1	8.58	0.010	0.9225	
A^2	395.45	1	395.45	0.46	0.5146	
B^2	1152.47	1	1152.47	1.36	0.2779	
C^2	140.15	1	140.15	0.16	0.6954	
AB	46.42	1	46.42	0.055	0.8211	
AC	60.81	1	60.81	0.071	0.7959	
BC	94.68	1	94.68	0.11	0.7472	
Residual	6803.90	8	850.49			
Lack of fit	3758.53	3	1252.84	2.06	0.2247	Not significant
Pure error	3045.36	5	609.07			
Cor. total	11173.73	17				

The model F-value both implied not significant to the noise with 0.64 for SPE-ester and 0.79 for UPE-ester. It was 64% (SPE-ester) and 79% (UPE-ester) chance that a model F-value this large could occur to this noise. Statistical model fit summary consisting of a sequential model sum of squares and lack of fit tests suggested a quadratic model as the best fit model. Values of Prob>F were not less than 0.05 indicated that the model terms were not significant in this case.

Correlation value (R^2) for SPE-ester was 0.47 which indicated that the model could explain 47% of the variability in esterification process. The negative predicted R^2 implied that the overall mean was a better predictor than the experimental response than the current model. The R^2 for UPE-esters was 0.39, and indicated that the model could explain 39% of the variability in the esterification process. The negative predicted R^2 implied that the overall mean was a better predictor than the experimental response than the current model. Selected models were inadequate for predicting the conversion of tetraesters, but the experimental results could be referred.

GC chromatogram is important in determining the production of esters in the synthesis of SPE-esters and UPE-esters (Figure 1).

Table 5. Composition of polyester and percent yield by weight in SPE-esters.

Run	Tetraester	Triester	Diester	Monoester	Percent yield (w/w)
1	40	21	39	-	65
2	43	12	45	-	55
3	60	9	32	-	51
4	1	3	89	3	51
5	76	15	9	-	69
6	57	-	44	-	57
7	47	-	53	-	61
8	2	4	94	-	63
9	42	15	42	-	36
10	19	9	71	-	63
11	2	3	79	15	57
12	1	9	84	6	57
13	16	6	70	8	60
14	9	2	81	8	68
15	65	10	25	-	62
16	35	17	48	-	58
17	51	49	-	-	67
18	9	6	83	-	70

Table 6. Composition of polyester and percent yield by weight in UPE-esters.

Run	Tetraester	Triester	Diester	Monoester	Percent yield (w/w)
1	40	21	39	3	79
2	43	12	45	-	67
3	60	9	32	-	81
4	3	3	91	2	72
5	76	3	21	-	61
6	-	44	-	56	77
7	-	53	-	47	74
8	2	4	94	-	50
9	42	15	43	-	83
10	19	9	71	-	82
11	2	3	79	15	69
12	1	9	84	6	75
13	16	6	70	7	70
14	9	2	81	8	59
15	65	10	25	-	75
16	35	17	48	-	62
17	51	-	49	-	37
18	9	6	85	-	75

The major tetraester was observed to be 76% for both esters (Table 7). The –OH group of PE was considered to be esterified as the formation of esters were shown in Figures 2 and 3 which agrees well by Noor and Jumat (2010) [20] as the peaks appeared were identified based on the number of fatty acids attached to the PE backbone. The products containing tetraester, triester, diester and monoester in SPE-esters (Figures 2 and Table 7) and UPE-esters (Figure 3 and Table 7) after the esterification reaction. All ester peaks are identified according to the carbon number of the alkyl groups attached to PE backbone by following the terminology used in fats and oils analysis [17].

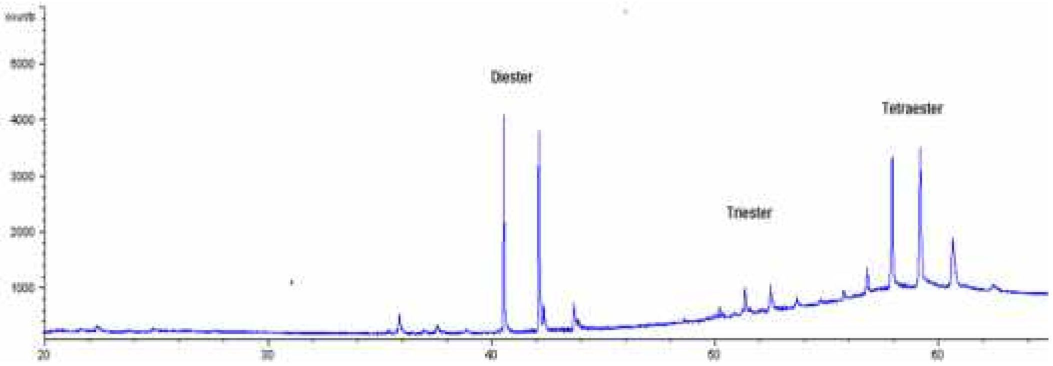


Figure 2. Gas chromatogram for SPE-esters.

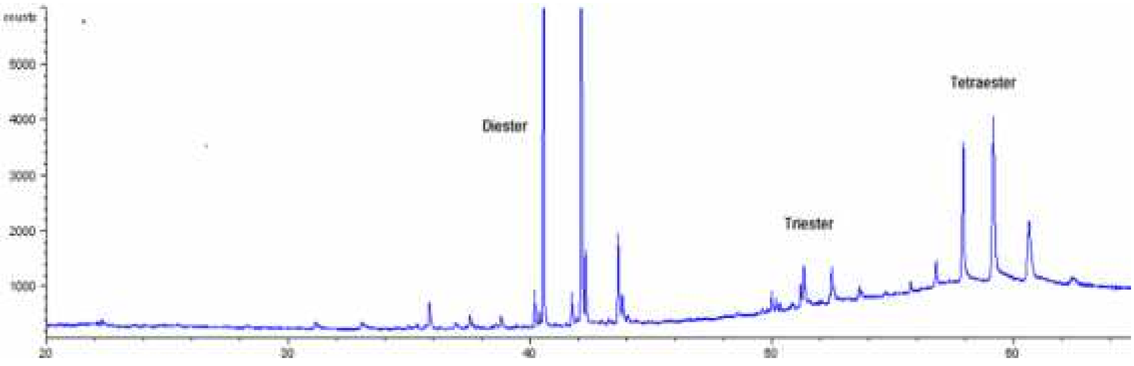


Figure 3. Gas chromatogram for UPE-esters.

Table 7. Composition of tetraester, triester, diester and monoester for SPE-ester and UPE-ester after esterification reaction.

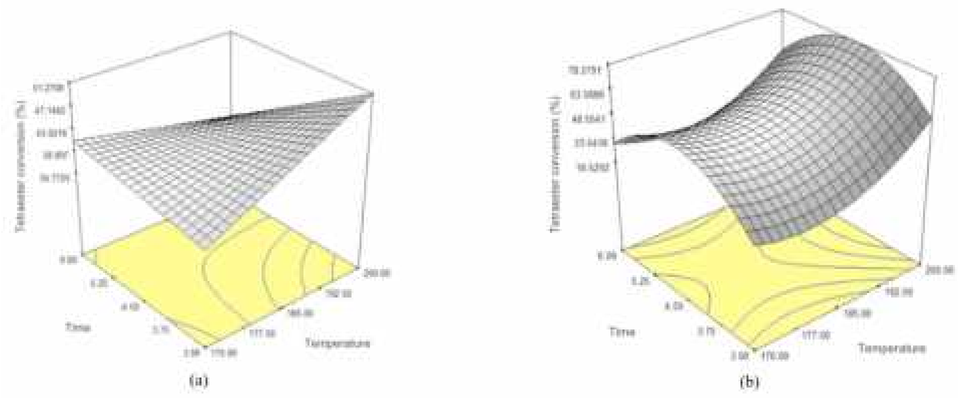
Products	SPE-ester (%)	UPE-ester (%)
Tetraester	76	76
Triester	15	3
Diester	9	21
Monoester	-	-

RSM was used in this study to evaluate the interactions between responses and variables. The model of esterification of SPE-esters and UPE-esters were based on the D-optimal design and the percentage of tetraester conversion was developed and analyzed by using RSM. The temperature-time, temperature-catalyst and catalyst-time are important parameter for the percentage of tetraester conversion for the production of ester. The ratio used was fixed for all parameters.

This process might help determine the best model for the reaction to reduce time and cost to produce the most optimum condition in the synthesis of both esters. The comparative data indicated that the esterification process depends on the conditions — time, temperature, catalyst, and the ratio to form ester linkage between SPSFA and UPSFA with PE.

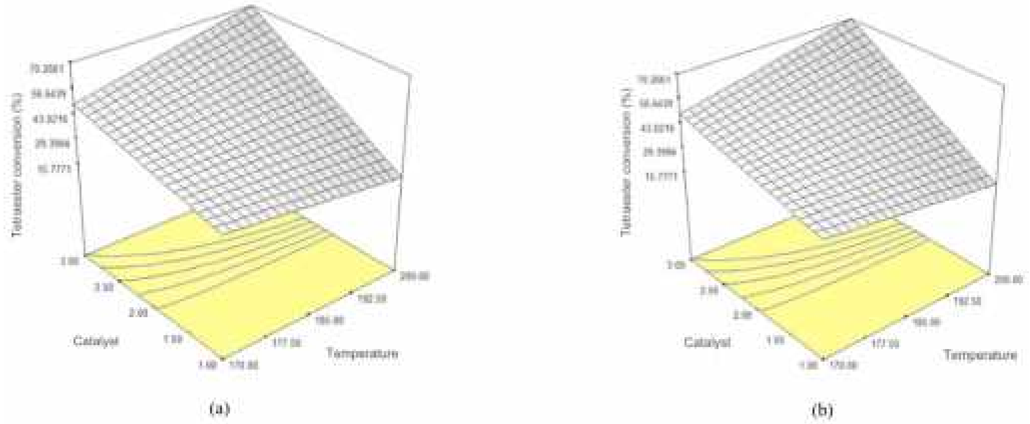
RSM was used in this study to evaluate the interactions between responses and variables. The relationships between independent (temperature, time, catalyst and SPSFA and UPSFA ratio) and dependent (response) variables are shown in the three-dimensional representation as response surfaces. The response surfaces effect of the temperature-time, temperature-catalyst and catalyst-time for the percentage of tetraester conversion is shown in Figures 4(a), 5(a) and 6(a) for SPE-ester and 4(b), 5(b) and 6(b) for UPE-ester, respectively.

Figures 4(a) and 4(b) show the effect of temperature and time on the tetraester conversion at a constant molar ratio of 5 for SPE-ester and UPE-ester. The reaction temperature for the UPE-ester influenced tetraester conversion compared to SPE-ester. Tetraester conversion was influenced by the



(a) (b)

Figure 4. Response surface effect of temperature (°C) and time (hour) on the tetraester conversion (%) in (a) SPE-ester and (b) UPE-ester.



(a) (b)

Figure 5. Response surface effect of temperature (°C) and catalyst (%) on the tetraester conversion (%) in (a) SPE-ester and (b) UPE-ester.

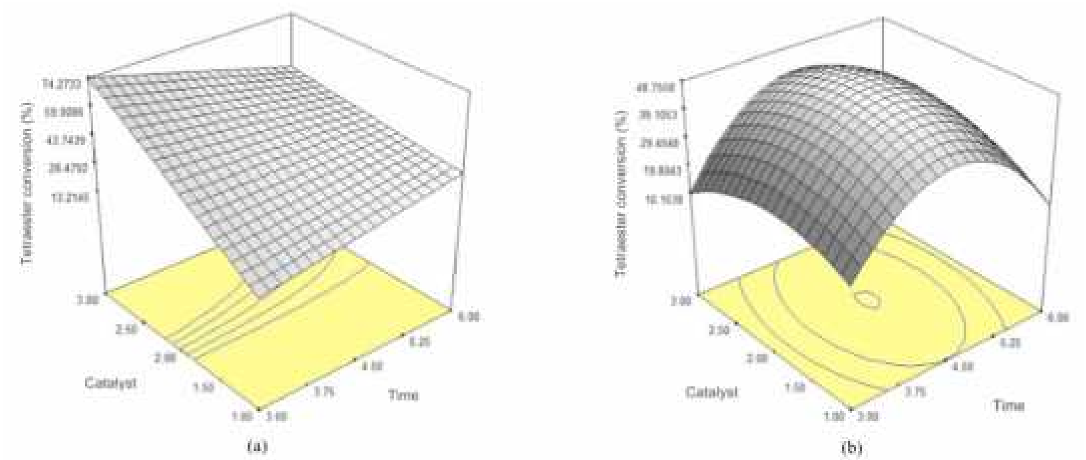


Figure 6. Response surface effect of catalyst (%) and time (hour) on the tetraester conversion (%) in (a) SPE-ester and (b) UPE-ester.

reaction temperature for UPE-ester compared to SPE-ester. Tetraester conversion of UPE-ester increases with an increase in reaction time. It signifies that temperature has a bigger effect on the tetraester conversion in UPE-esters.

The effect of catalyst and time on the tetraester conversion at a constant molar ratio of 5 for SPE-ester and UPE-ester are shown in Figures 6(a) and 6(b). Tetraester conversion was influenced significantly by the catalyst loading for SPE-ester compared to UPE-ester. Tetraester conversion of SPE-ester increases with a decrease in reaction time. It signifies that catalyst loading has bigger positive effect on the tetraester conversion in SPE-ester.

The important infrared peaks are illustrated in Figures 7 and 8. The sharp peak of v(C=O) stretching band shifted from 1696 cm^{-1} (SPSFA) and 1710 cm^{-1} (UPSFA) to 1742 cm^{-1} for SPE-ester and UPE-ester, respectively to prove the formation of both esters after esterification. The v(OH) broad peak did not appeare in the PE-ester spectra to confirm carboxyl groups in SPSFA, and UPSFA is successfully esterified with hydroxyl groups of the polyhydric alcohol (PE). The peak of C=C did not exist in SPSFA and SPE-ester as it existed in UPSFA and UPE-esters as only unsaturated fatty acids consisting of double bonding.

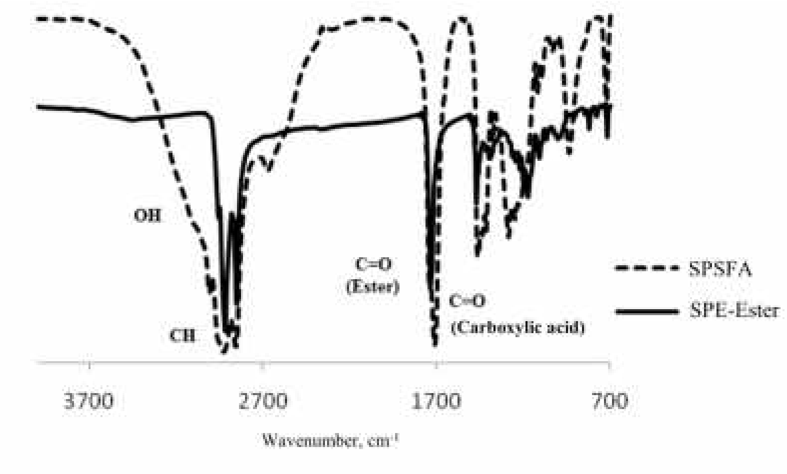


Figure 7. The comparison of IR peaks for SPSFA and SPE-ester.

Table 8. Comparison of IR peaks for SPSFA and SPE-ester.

Functional group	SPSFA peak (cm^{-1})	SPE-esters peak (cm^{-1})
-OH stretch	3400-2400	-
CH-sp^3 stretch	2926, 2856	2925, 2856
C=O stretch	1696	1742
CH_2 bend	1470	1462
CH_2 long chain	721	722

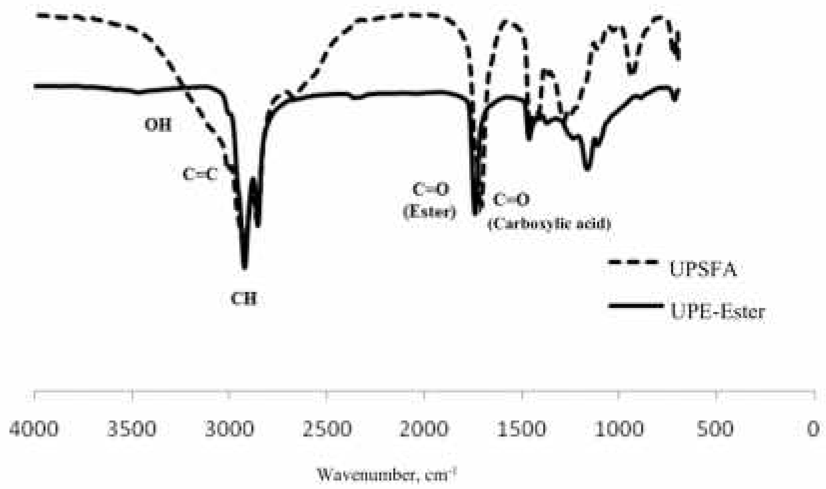


Figure 8. The comparison of IR peaks for UPSFA and UPE-ester.

Table 9. Comparison of IR peaks for UPSFA and UPE-ester.

Functional group	UPSFA peak (cm^{-1})	UPE-esters peak (cm^{-1})
-OH stretch	3400-2400	-
C=C	3001	3001
CH-sp^3 stretch	2926, 2856	2925, 2855
C=O stretch	1710	1742
CH$_2$ bend	1469	1463
CH$_2$ long chain	721	723

The ^{1}H NMR spectrum are shown in Figures 9 and 10 for proton signals, and carbon signals are shown in Figures 11 and 12 for both esters. Chemical shifts, δ in ppm for both esters are tabulated in Table 10 for proton, and Table 11 for carbon.

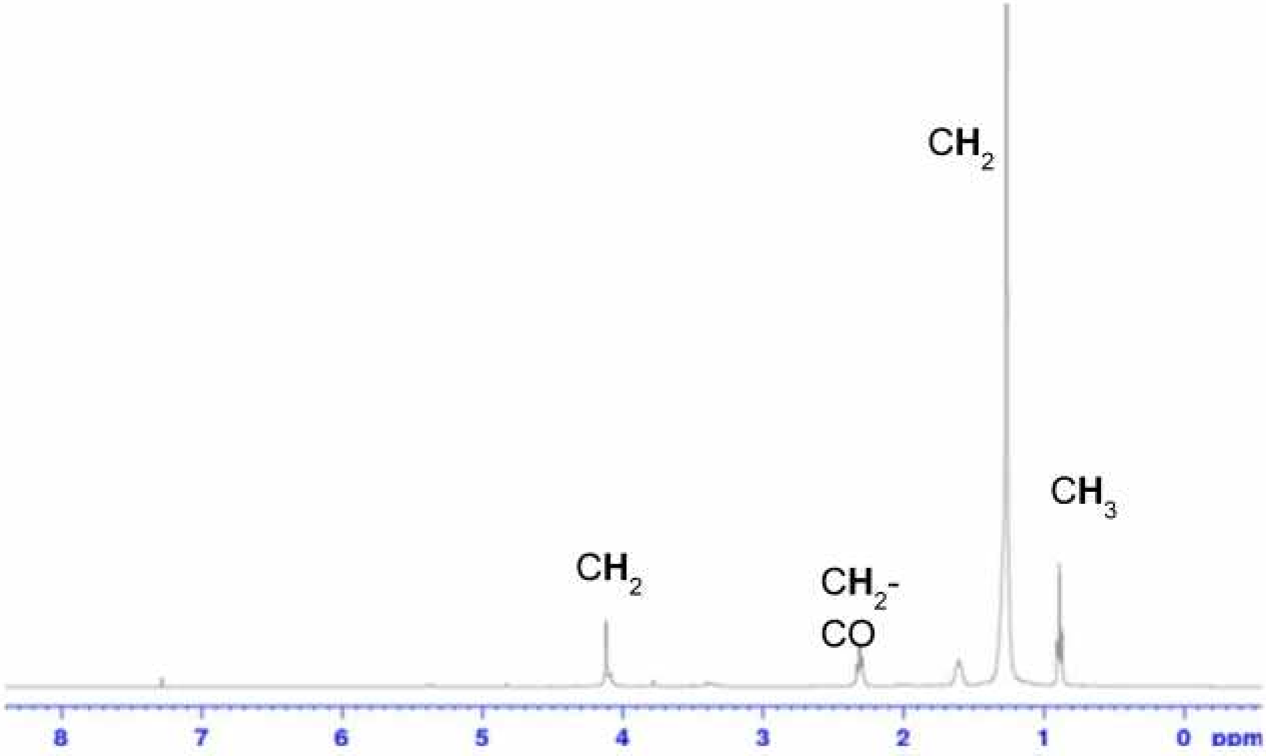


Figure 9. ^{1}H NMR spectrum for SPE-ester.

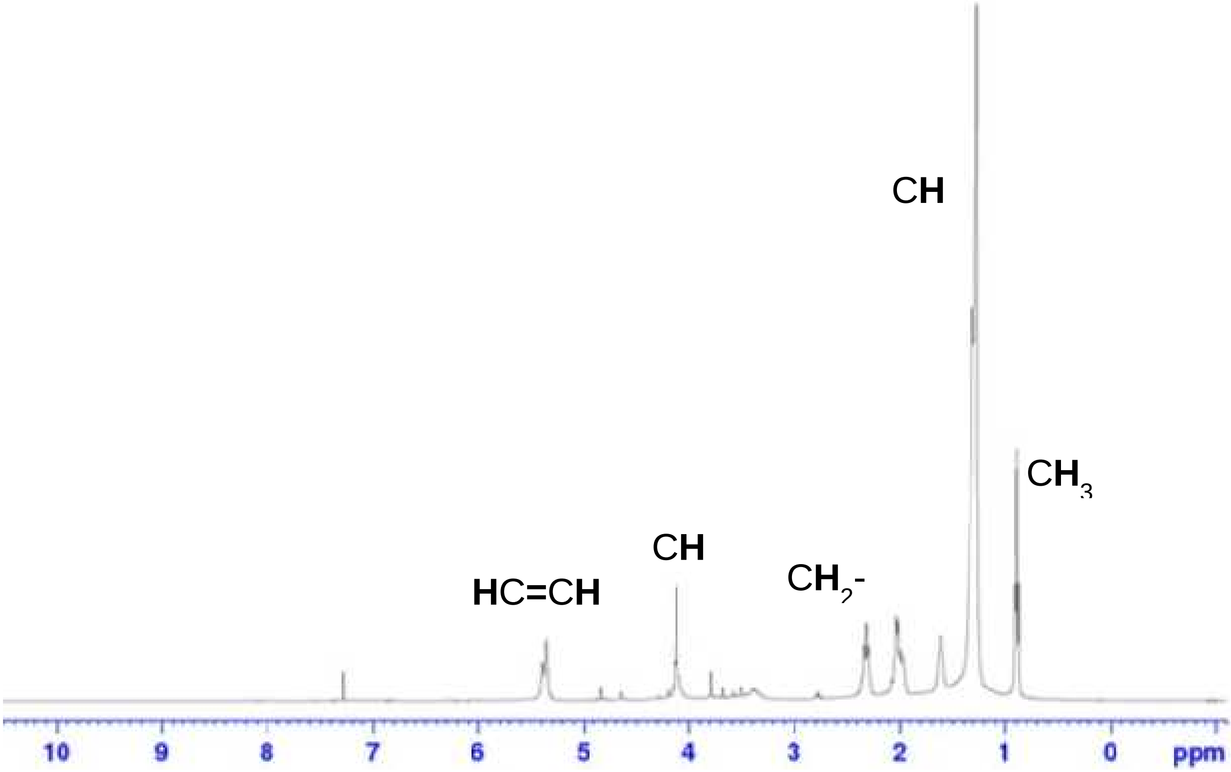


Figure 10. ^{1}H NMR spectrum for UPE-ester.

The ^{1}H NMR spectrum provides significant peaks in determining the structure of SPE-ester and UPE-ester (Figure 1). The analysis found that the signals of C**H**$_2$-O as the major ester group in SPE-ester and UPE-ester were at 4.83 and 4.09 ppm, respectively. The most apparent proton signal is **H**C=C**H** as it appears at 5.34 ppm in Figure 10.

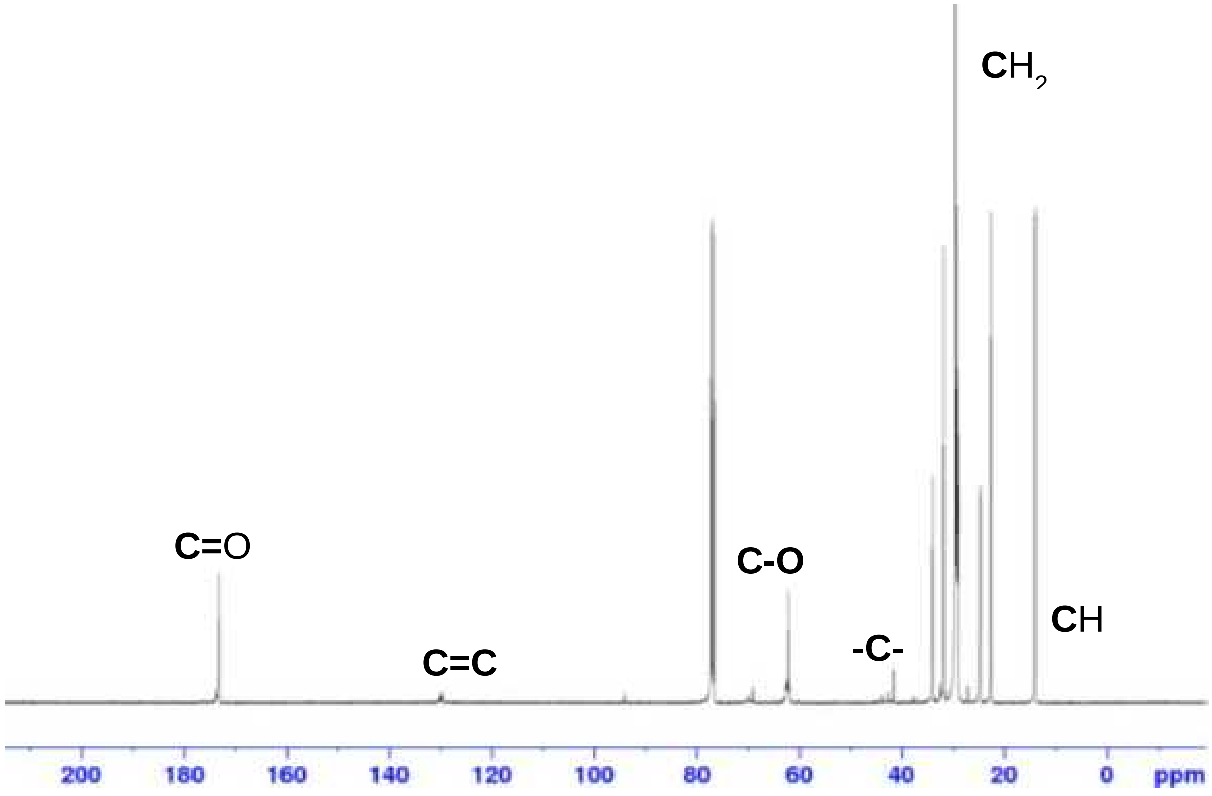


Figure 11. ^{13}C NMR spectrum for SPE-ester.

Table 10. Chemical shifts, δ in ppm for SPE-ester and UPE-ester.

Type of proton	SPE-ester (ppm)	UPE-ester (ppm)
CH_2-O	4.83	4.09
CH_2C=O	2.81-2.35	2.25-2.30
CH_3	0.88-0.85	0.89-0.88
CH_2 (long chain)	1.62-1.22	1.62-1.27
HC=CH	-	5.34
CH_2-O	4.83	4.09

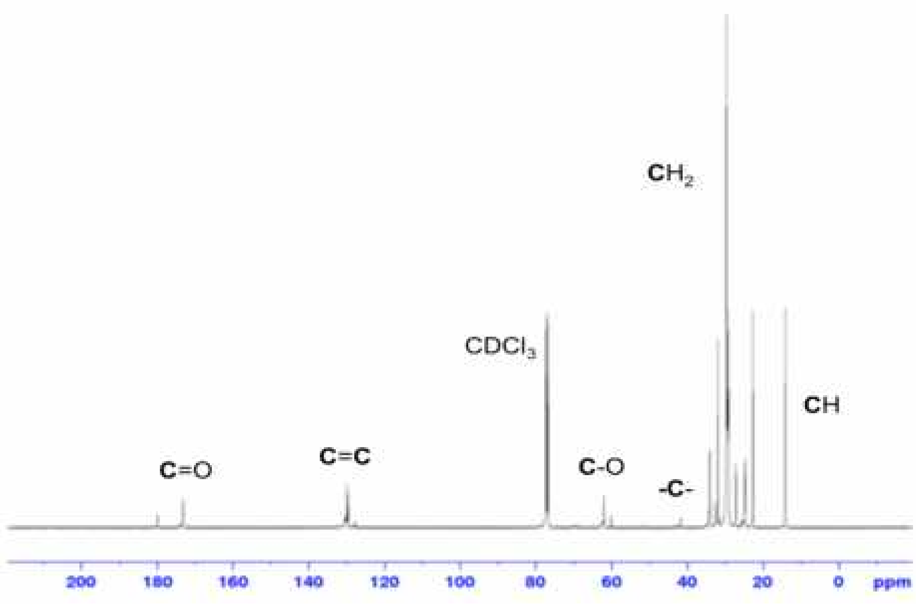


Figure 12. ^{13}C NMR spectrum for UPE-ester.

Table 11. Chemical shifts, δ in ppm for SPE-ester and UPE-ester.

Type of carbon	SPE-esters (ppm)	UPE-esters (ppm)
C=O	173.29	173.27
C=C	130.29	130.01
C-O	70.01-62.19	69.19
-C-	34.09	34.08
CH_2 (long chain)	21 24-22.71	33.62-22.70
CH (terminal)	14.13	14.14
CH_2	22.97	22.70

The ^{13}C NMR spectrum for SPE-ester (Figure 11) and UPE-ester (Figure 12) are important in the determination of SPE-ester and UPE-ester structure. The most important signal to show the production of esters is the ester carbonyl, **C**=O signal at 173.29 ppm (SPE-esters) and 173.27 ppm (UPE-esters). From the interpretation of IR (Figures 7 and 8), ^{1}H NMR (Figure 9) and ^{13}C NMR (Figure 10) spectrum, both ester structures were obtained as expected. However, a very small signal detected at 173.29 ppm in Figure 11 indicated that **C**=**C** slightly existed in SPE-ester.

Physicochemical Properties for RBDPS, SPE-esters and UPE-esters

Several physicochemical properties were studied in the preparation of both esters as biolubricant basestocks (Table 12). These studies showed improvement of the TAG in RBDPS after it was esterified with PE in the synthesis of SPE-esters and UPE-esters.

Table 12. The physicochemical properties between RBDPS, SPE-esters and UPE-esters.

Sample	RBDPS	SPE-esters	UPE-esters
Pour point (°C)	37	44	9
Flash point (°C)	190	243	232
Fire point (°C)	212	260	260
Kinematic viscosity at 40°C (cSt)	300	163	114
Kinematic viscosity at 100°C (cSt)	10	27	35
Viscosity index	-2	140	151
Oxidative stability (°C)	190	269	238

The pour point of UPE-esters which consisted of unsaturated fatty acid was lower than that of SPE-esters which consisted of saturated fatty acid. This was due to the liquid state of UPE-esters at room temperature compared to SPE-esters in the form of solid. Moreover, complex structures with branched ester possessed lower pour point. The branched chain could improve the temperature lubricity properties at low temperature and also the hydrolytic stability. In this study, it was observed that UPE-esters (44°C) had a lower pour point compare to SPE-esters (9°C).

From this study, the flash point of SPE-esters and UPE-esters were recorded at 243°C and 232 °C. Both esters had a higher flash point compared to RBDPS. The number of carbons in that particular molecule played a big role in influencing the flash point temperature. The higher value indicated that SPE-esters and UPE-esters were suitable as a lubricant. Unsaturated fatty acid is commonly less resistant to oxidation at high temperature and easily oxidized. The reaction of the unsaturated chain (C=C) with oxygen will form free radical that lead to polymerization and fragmentation of ester into acid an olefin. However, the symmetrical structure of both esters cause the molecular configuration less effective in retarding molecule packing which will improve the lubricity properties for both esters. Besides, the oxidative stability for both esters increases with the onset temperature recorded, which was 269°C (SPE-esters) and 238°C (UPE-esters). As expected, UPE-esters with a high degree of unsaturation will have a lower onset temperature compare to SPE-esters. Moreover, the advantage of both esters to possess symmetrical structure due to chemical modification with PE, which encourages the free radical to undergo cleavage, fragmentation, and polymerization.

CONCLUSION

SPE-esters and UPE-esters were successfully synthesized with high conversion of tetraester after esterification of SPSFA and UPSFA with PE using sulphuric acid as catalyst. The characterization results obtained has confirmed the production of both esters. Pour point, flash point, fire point, viscosity index, and oxidative stability of both esters proved to show improvements in the physicochemical studies and had high potential in the industry of biolubricant, and were able to achieve *ISO* grade lubricant. SPE-esters and UPE-esters produced were compatible to *1S0 VG 46/150* and *ISO VG 100/150*, respectively.

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