D-Optimal Design Optimization for Esterification of Palm Fatty Acids Distillate with Polyhydric Alcohols for Biolubricants Production

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ABSTRACT: *Plant-based bio-lubricant is crucial to be developed and adopted by many industries. This is due to the presence of toxicity risk, climate change, energy security as well green-environmental approach issues. The utilization of palm oil processing industries' by-product, palm fatty acid distillate (PFAD-based bio-lubricants is one way of a green environment approach. A synthesis of polyol esters based on PFAD for bio-lubricants was carried out. The esterification of PFAD with high-degree polyhydric alcohols trimethylolpropane (TMP), di-trimethylopropane (di-TMP), pentaerythritol (PE), and di-pentaerythritol (Di-PE) in the presence of sulphuric acid (H_2SO_4) catalyst have been performed. The optimization of the esterification reaction process was evaluated using a D-optimal design based on three reaction parameters; H_2SO_4 concentration (%) for the catalyst, esterification time (h), and esterification temperature (°C). The chemical structure of the synthesized polyol esters was characterized and confirmed by using FT-IR and NMR (^{1}H and ^{13}C) spectroscopies. The results showed that PFAD-based polyesters of PFAD-TMP ester successfully produced high yields of 93% compared to others. The synthesized PFAD-based polyesters showed good lubrication properties with high viscosity indices in the range of 141-187, pour points (-5 to 5 ºC), flash points (230-360 ºC), and oxidative stability temperature (188-301 °C), respectively. The ester functional group present in the chemical structure of PFAD-based polyesters showed a positive impact on the lubrication properties. The study indicated that PFAD-based polyesters are plausible to be used in industrial bio-lubricant applications.*

KEYWORDS: *Palm fatty acid distillate; D-optimal design; Biolubricants; Response surface methodology*

INTRODUCTION

In recent years, increasing awareness about environmental issues and global climate change has shifted the attention of using petroleum-based materials towards more biodegradable and renewable materials. At the same time, for example, stringent regulations by the government have accelerated the adoption of plant-based lubricants. High biodegradability together with the low toxicity and the availability of plant-based oils has made them

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a lucrative candidate as an alternative for biolubricant feedstock [1, 2]. Lubricants produced from plant oils are classified as good biolubricants due to their many advantages compared to petroleum-based lubricants. They are biodegradable, non-toxic to humans and other living organisms, have no adverse effects on the environment, and are cheaper in price [3]. Other advantages include low volatility, good lubrication, and good anti-corrosion properties [4, 5]. However, plant oil-based biolubricants occupy two major problems; inadequate oxidative stability and low fluidity at low temperatures [6] due to their unsaturated to saturated acyl groups ratio. Proper chemical modification to convert plant oils to plant-based biolubricants is an attractive slick way to solve these problems [7-10]. Many studies have reported on the production of plant oil or their derivatives-based biolubricants. Most plants-oil based biolubricants have traditional oxidative issues due to their β-hydrogen presence in their glycerol backbone triacylglycerols. This problem could be overcome by replacing the glycerol backbone with any polyhydric alcohols such as TMP, PE *via* transesterification with plant oil Fatty Acids Methyl Esters (FAME). Direct transesterification with plant oil such as palm oil and trimethylolpropane (TMP) has been reported. The production of biolubricant *via* transesterification of palm oil methyl ester (POME) with TMP was reported by *Aziz et al*. 2020 [11] and *Cecilia et al*. 2020 [6]. The result showed 86% of palm oil TMP triesters were successfully synthesized. Most of the studies used POME as a starting material in transesterification with TMP. However, fewer studies have reported the use of Palm Oil Fatty Acids (POFA) *Fadzil et al*. 2019 [12], *Nor et al*. 2019 [13], as a starting material in the esterification process.

Plant oil fatty acids such as Palm Oil Fatty Acids (POFA) and Palm Fatty Acids Distilled (PFAD) have less attention to being used for biolubricants, *Fernandes et al*. 2018 [14], *Jumaah et al*. 2019 [15]. PFAD is a by-product and less valuable material from the crude palm oil refining process. PFAD is a light brown semi-solid at room temperature melting to a brown liquid on heating. PFAD comprises mainly mixtures of Free Fatty Acid (FFA) (>80%). These large amounts of Free Fatty Acid (FFA) in PFAD have been recovered during the deodorization process. Oleochemical industries have found ways to utilize this cheap raw material PFAD for animal feed [16-18], as the raw material for intermediate products of soap and medium-grade cleaners [15, 18]. PFAD is also used as a firelighter [19]. Some researchers also point toward the promise of using FFA extracted from PFAD as biodiesel [20, 21]. PFAD is also used as raw material to make plastic [22]. PFAD for the synthesis of organic esters for plasticizers [23]. However, PFAD has little use in industry for the production of high-end products such as green biolubricants. Few reports on the potential of using PFAD for the production of environmentally benign polyol esters through non-conventional catalysis or enzymatic process for biolubricants [14, 24] with limitations due to the selectivity of the enzyme used towards the type of fatty acid involved in the esterification process. However, the uniqueness and advantages of palm fatty acids distilled (PFAD) in producing biolubricant can be enhanced by using the conventional chemical catalyst such as a mineral acid catalyst. This is due to PFAD having a significantly high composition of saturated palmitic acid at 48.9% and unsaturated oleic acid at 37.4% and linoleic acid at 11%. The high percentage of saturated palmitic acid of PFAD produces high stability properties to the biolubricant. Furthermore, the good composition of unsaturation oleic acid in PFAD could produce better cold flow properties to the lubricants, and its suitable for industrial uses. Through selective chemical modification, the stability of these saturated and unsaturated-chain esters will improve thermal and oxidative stability while lubricity and viscosity index is maintained [20, 25, 26].

Response surface methodology (RSM) was used in many studies for the optimization of the process such as the esterification of fatty acids and polyhydric alcohols. One of the reliable common RSM modes of optimization is D-optimal design. D-optimal designs are generated for multi-factor experiments with both quantitative and qualitative factors. D-optimal designs are constructed to minimize the overall generalized variance of the estimated regression coefficients. As a result, the 'optimality' of a given D-optimal design is model-dependent. Therefore, using a D-optimal design for the optimization of esterification reactions of free fatty acids in PFAD with any alcohols will be cost-effective by reducing the number of experiment numbers.

The aim of this work was to synthesize polyol-ester using acid-catalyzed esterification reactions of PFAD with different kinds of polyhydric alcohols (trimethylolpropane

(TMP), di-trimethylopropane (Di-TMP), pentaerythritol (PE) and di-pentaerythritol (Di-PE) to produce green biolubricants. Polyhydric alcohol is preferred since it does not contain β–hydrogen, which heightens the biolubricant's thermal and oxidative stability at high temperatures. This paper details the practical use of The D-optimal method is a design of an experiment to optimize the esterification reactions of PFAD with polyhydric alcohols. The effects of different process conditions with regard to the responses were optimized and determined with the assistance of Response Surface Methodology (RSM). In the end, this work finds better research and development towards boosting the industrial potential usage of cheap raw material of PFAD, which thus increase the value-added of PFAD in the market.

EXPERIMENTAL SECTION

Materials

In this study, Palm Fatty Acid Distillate (PFAD) was obtained from a local refinery, Sime Darby Plantation Berhad (647766-V), located in Selangor, Malaysia. Polyhydric alcohols, toluene, sulphuric acid (97%), sodium bicarbonate, ethyl acetate, sodium chloride, and anhydrous sodium sulfate were purchased from Sigma Aldrich (Steinheim, Germany). All the chemicals used in this study were either analytical or High-Performance Liquid Chromatography (HPLC) grade and used directly without further purification.

Structural characterization analysis

Determination of fatty acid composition was performed using a Shimadzu GC-17A Gas Chromatography (GC), equipped with a capillary column BPX 70 (30m × 0.25mm ×0.25 m) and FID detector. The column temperature was programmed to 120°C, which was gradually raised as much as 3 °C, every 1 min for 57 min. The injector and detector temperatures were set at 260 and 280 °C, respectively. Helium gas as the carrier gas was used with a flow rate of 0.3 mL/min. The parameters of GC were carried out according to *Derawi* and *Salimon* (2014) [27]. The structure of synthesized compounds was confirmed and determined using Nuclear Magnetic Resonance (FT-NMR) and Fourier Transform InfraRed (FT-IR) spectroscopy. FT-NMR (^{1}H and ^{13}C NMR) analyses were recorded on JEOL-ECP 400 spectrometer using $CDCl_3$ as the solvent. The FT-IR spectra were recorded on a Perkin Elmer Infrared Spectrophotometer within the range between 500 and 4000 cm^{-1}.

Lubrication characterization analysis

The American Society for Testing Materials standards (ASTM) was used to determine the lubrication characteristics. For certain, ASTM D-6186 of oxidative stability [28], ASTM D-97 of pour point [29], and ASTM D-93 of flash point [30]. The Oxidative Stability Temperature (OST) in the current study was carried out using Pressurized Differential Scanning Calorimetry (PDSC822e, Metter Toledo), which is a highly-selected device to evaluate the Oxidative Stability Temperature (OST) of oleochemicals. A rheometer with model physical MCR 301 from Anton Paar Instruments (Germany) was used to measure kinematic viscosity. The viscosity and viscosity index were calculated according to ASTM D-2270 method [31, 32]. All the measurements were performed in triplicate and the data was reported as a mean ± SD of triplicate determinations.

Esterification reaction

Biolubricant was synthesized from the esterification reaction between fatty acids with various high-degree polyhydric alcohols. In a flask with a reflux condenser and three necks, fatty acids were mixed with polyhydric alcohol in 20-30 mL of toluene as an azeotropic distillation agent. The Dean-Stark distillation method was referred to carry out the esterification in this study. To reach the 110-200 °C experimental temperature, an oil bath with a magnetic heater was used, and the mixture was put into it and stirred. This was followed by the addition of concentrated H_2SO_4 of 1–5% (as a percentage of the weight of fatty acid) before the reaction. Then, the flask was allowed to cool to room temperature upon reaction completion, followed by the removal of toluene with a rotary evaporator at 100 °C. After heating was stopped, the product from the reaction was left to cool at room temperature. This was followed by the dissolution of the cooled reaction product with ethyl acetate (25mL), and the product was transferred into100mL the separation funnel then added 10 mL saturated sodium bicarbonate ($NaHCO_3$) and shook. The funnel was left until two layers formed. The aqueous layer at the bottom was removed, leaving the organic layer then $NaHCO_3$ was used to wash the organic layer three times. Subsequently, 10 mL of saturated sodium chloride (NaCl) and 10 mL of distilled water were used to wash the mixture twice to avoid any form of an emulsion. Once the two layers are formed, the bottom layer was removed. Washing was repeated until a solution with pH 7 was obtained. Then, the washed sample was poured

Table 1: Independent variables and levels of D-optimal design for the esterification reactions.

Independent variables	Factor X_i	Variable levels		
		-1	0	1
H_2SO_4 concentration (%)	X_1	1	3	5
Esterification time (hr)	X_2	2	4	6
Esterification temperature (°C)	X_3	110	130	150

Table 2: Experimental runs of D-optimal design and response for the esterification reactions.

Run No.	Variables levels, X			Responses, Y	
	X_1	X_2	X_3	Y_1	Y_2
1	5	4	150	88	91
2	5	2	150	67	78
3	1	6	110	80	88
4	5	2	110	59	67
5	1	6	150	78	78
6	3	4	110	87	88
7	5	6	110	79	87
8	1	2	150	60	70
9	3	6	130	90	97
10	1	2	110	53	62
11	4	3	130	93	99
12	5	6	150	87	86
13	1	4	130	90	98
14	3	2	150	71	74
15	1	6	110	75	86
16	5	6	110	81	84
17	1	6	150	77	80
18	1	2	110	52	63

Notes: X_1= Acid catalyst (%); X_2 = Time (hr); X_3 = Temprature (°C); Y_1 = Yield (%); Y_2 = Tri-ester (%)

into a round flask and connected to a rotary evaporator apparatus (90-100 °C) to remove any excess toluene and unreacted alcohol. Next, the sample was placed in a small beaker, and sodium sulfate (Na_2SO_4) was added to absorb the remaining water in the sample. The hydrated Na_2SO_4 was filtered off before the sample was poured into a sample bottle.

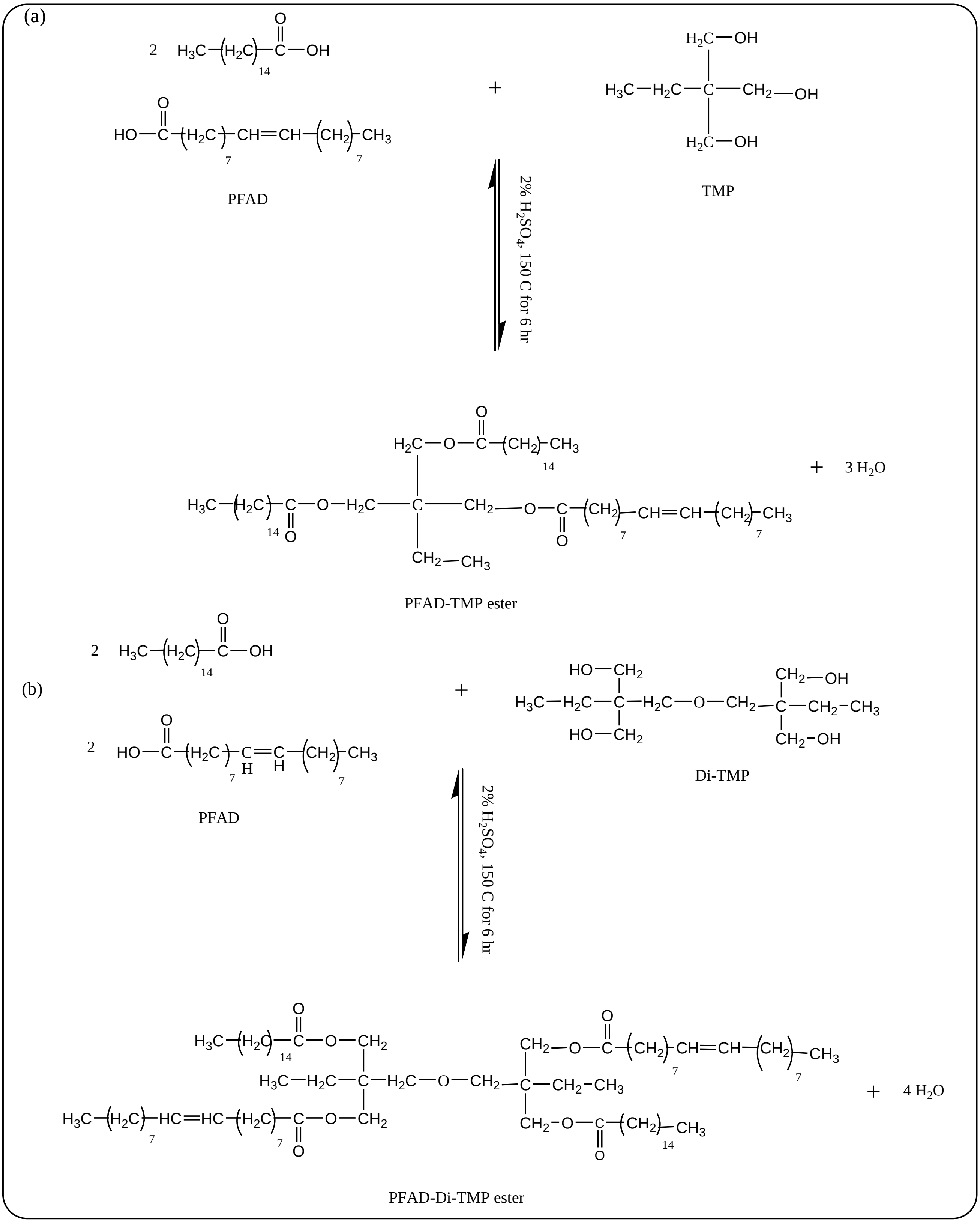
Statistical analysis and experimental design

To assess the reaction of the synthesized biolubricat, this study employed a three-factor D-optimal design. Biolubricant yield Y_1 (%) and concentration of triester Y_2 (%) were determined using the D-optimal experimental design generating 18 runs, as presented in Table 2. The independent variables were denoted as X_1 for H_2SO_4 (%) concentration (as a percentage of the weight of fatty acid), X_2 for esterification temperature (°C), and X_3 for esterification time (hr). The low value (-1) and high value (+1) of X_1, X_2, and X_3 as can be seen from Table 1 were equivalent to the range setting of each parameter: 1- 5% for X_1, 2- 6 hr for X_2 and 110-150 °C for X_3.

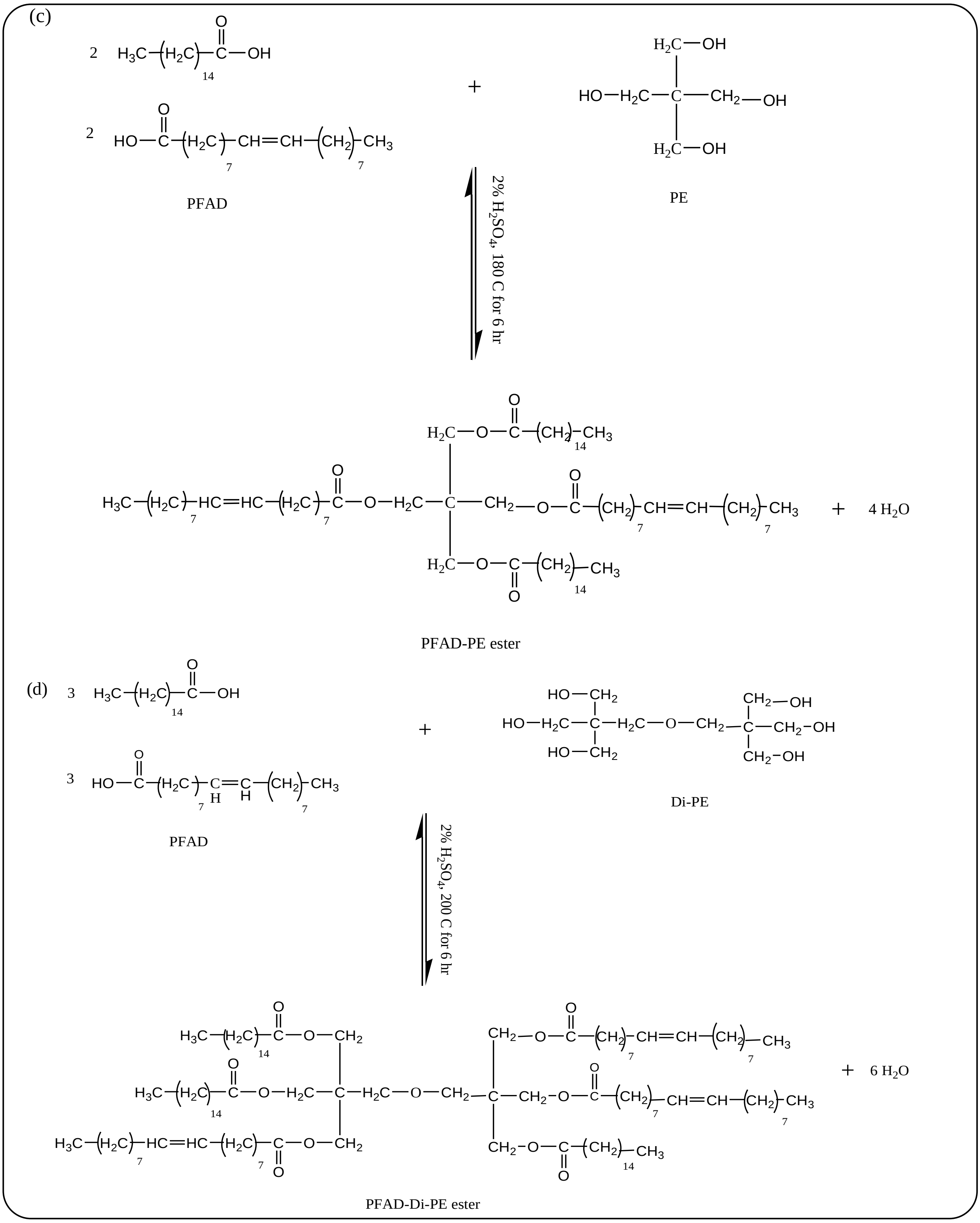
RESULTS AND DISCUSSION

Esterification of PFAD

PFAD was separately reacted with selected four high-degree polyhydric alcohols to produce four PFAD esters, known as PFAD-TMP ester; PFAD-Di-TMP Ester; PFAD-PE ester; and PFAD-Di-PE ester. For discussion simplicity, PFAD is well represented by its major palmitic and oleic acids. The schematic chemical reaction for the synthesis of PFAD-polyhydric alcohol-based esters are shown in Scheme 1 (a, b, c, and d), respectively.



Scheme 1: Schematic chemical reaction for the synthesis of polyol esters (a) PFAD-TMP; (b) PFAD-Di-TMP; (c) PFAD-PE and (d) PFAD-Di-PE.



Scheme 1: Schematic chemical reaction for the synthesis of polyol esters (a) PFAD-TMP; (b) PFAD-Di-TMP; (c) PFAD-PE and (d) PFAD-Di-PE.

Response surface methodology

The optimum condition and high percentage of yield production were determined using response surface methodology (RSM). This method is also used to improve the physical properties of the biolubricant. In this study, the D-optimal design for the experiments was used, for example, to optimize the esterification reaction of PFAD with TMP to synthesize ester TMP. The yield of ester TMP and the yield and percentage of tri-ester in ester TMP were investigated using a three-factor D-optimal design. The effects of different process conditions on the responses were optimized and determined using RSM. The response factors and values were determined *via* an initial screening step. In this step, X_1, X_2, and X_3 were used to represent the catalyst (mL/g), Time (h), and temperature (°C), respectively. While the molar ratio was selected from manual optimization to be 3.5:1 (PFAD:TMP), each variable was evaluated by varying its values within a minimum and maximum value, as presented in Table 1. The experimental data of the yield and tri-ester percentage of all the samples are provided in Table 2.

D-Optimal design model fitting

A quadratic polynomial model represents the relationship between the independent variables and the percentage of the yield of ester and the percentage of tri-ester in ester-TMP. Equations (1) and (2) provide the coefficients to estimate the model using the experimental results as a basis.

$$Y_1 = +98.13 + 2.98X_1 + 9.79X_2 + 2.65X_3 - 0.4894X_1X_2 + 0.6884X_1X_3 - 1.42X_2X_3 - 5.54X_1^2 - 14.41X_2^2 - 8.34X_3^2 \quad (1)$$

$$Y_2 = +102.06 + 2.27X_1 + 7.33X_2 + 1.08X_3 - 1.11X_1X_2 + 1.42X_1X_3 - 3.27X_2X_3 - 1.03X_1^2 - 10.96X_2^2 - 13.45X_3 \quad (2)$$

The responses, Y_1 and Y_2, are the yield, and percentage of tri-ester, respectively. The variables X_1, X_2, and X_3 respectively represent the acid catalyst (mL/g), time (h), and temperature (°C). Tables 3 and 4 show the analysis of variance (ANOVA) for this regression model. The independent variable range described all models, P-values (< 0.0001) indicated that the models significantly describe the esterification of PFAD with an adequate precision of 19.8376 and 27.2895 for Y_1 and Y_2, respectively. The adequacy of the signal-to-noise ratio was considered desirable with a value greater than 4 [33]. Model Y_1 (yield of ester) and Y_2 (percentage of tri-ester) were reasonably significant with all variables X_1, X_2, and X_3 exhibiting $p < 0.05$ (Tables 3 and 4). The lack of fit for all models is shown by P-values of 0.20 and 1.03, indicating the models are insignificant relative to the pure error [34]. From Tables 3 and 4, it is clear that every three responses have a significantly high R-squared (R^2) and adjusted R-squared (R^2-adj) correlation coefficients, showing that the values from the experiment are in agreement (have a good fit) with the regression model.

Adequacy checks of the model

An adequacy check was employed to check the model's accuracy. This is important because a valid mathematical model with high accuracy would enhance the real process while an inaccurate model may give poor or false results. The studentized residuals were plotted against the predicted yield and the percentage of triester as highlighted in Fig. 2. Studentized plots of residual *vs* the value of a fitted response shows off the distribution of points that is scattered about the boundary of 0 to ± 4.506 at random, suggesting that the variance is constant for all response values. Thus, it is confirmed that the models are suitable for application without any transformations to reduce the scatter [33, 34]. Conversely, Fig. 3 showed the distribution of plots of the actual data against the predicted values of yield, and percentages of tri-ester. The preliminary experimental results in Table 2 were used as actual data, while the model provided the predicted data. It is discernible that all data points cluster around the line, which indicates the models fit with the empirical data. Therefore, the models should be able to predict yield and the percentages of tri-ester that concur remarkably with the real experimental values. This was statistically confirmed by the values of R^2 and R^2adj, as shown in Tables 3 and 4, indicating a reliable prediction of results. Hence, it was desirable to progress to the next stage of analysis using the optimization tool.

Response surface analysis and optimization conditions

The esterification of PFAD with TMP involves many variables, the interaction of which is investigated using 3-D response surfaces and contour graphs. The response

Table 3: Analysis of variance (ANOVA) of yield (Y_1) and tri-ester percentage (Y_2) of PFAD-TMP ester.

Source	Sum of Squares	F-Value (Y_1)	P-value (Y_1)	F-Value (Y_2)	P-value (Y_2)	Status
Model	2819.49	42.16	< 0.0001	78.63	< 0.0001	Significant
X_1	114.15	15.36	0.0044	21.37	0.0017	
X_2	1227.53	165.18	< 0.0001	222.67	< 0.0001	
X_3	99.99	13.45	0.0063	5.33	0.0498	
X_1X_2	2.67	0.3599	0.5651	4.42	0.0688	
X_1X_3	5.76	0.7751	0.4043	7.90	0.0228	
X_2X_3	24.63	3.31	0.1062	42.10	0.0002	
X_1^2	64.55	8.69	0.0185	0.7243	0.4195	
X_2^2	436.80	58.78	< 0.0001	81.72	< 0.0001	
X_3^2	118.53	15.95	0.0040	99.70	< 0.0001	
Residual	59.45					
Lack of Fit	43.95	2.84	0.1685	1.75	0.3005	Not significant
Pure Error	15.50					
Cor Total	2878.94					

Notes: $R^2 = 0.9793$; $R^2adj = 0.9561$; Adequate precision = 19.8376; Significant at $P < 0.05\%$ level; X_1 = Acid catalyst (%); X_2 = Esterification time (hr); X_3 = Esterification temperature (°C).

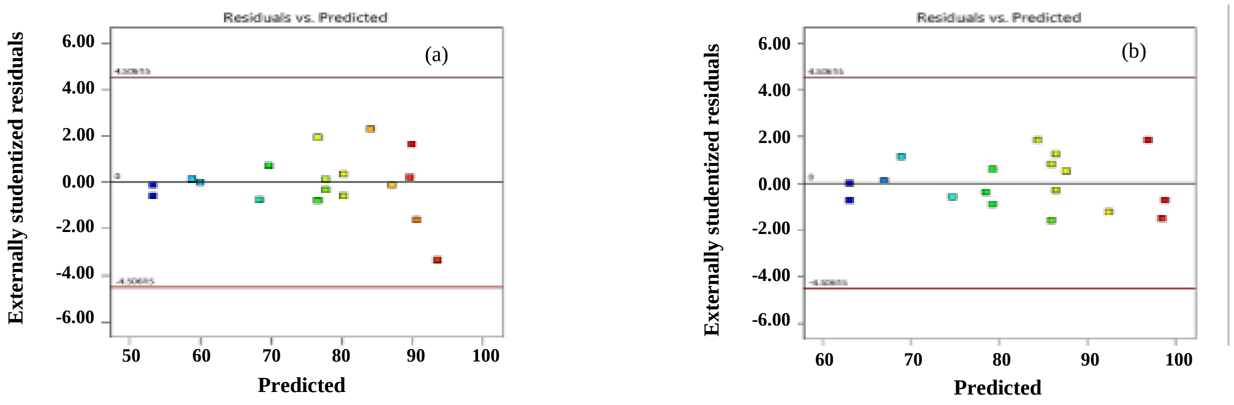


Fig. 2: Studentized residuals versus the predicted value for (a) yield of ester and (b) tri-ester percentage.

surfaces for the yield (Y_1) and tri-ester percentage (Y_2) are given in Figs. 4 (a-c) and 5 (a-c), respectively. The maximum yield at 93.3% was obtained at an acid catalyst of 5% and a time of 5 h (Fig. 4a). The 3D graph shows that the maximum yield of PFAD-TMP ester was obtained at an acid catalyst of 5% and a temperature of 145 °C (Fig. 4b). The combined effect of time and temperature demonstrated that ester yield increased with an increase in time (Fig. 4c). The interaction effect between the acid catalyst and time is shown in Fig. 5a. The 3D plot shows that increasing the ratio of acid catalyst from 1-5% continuously improved the tri-ester of PFAD-TMP ester, while the optimal time for the maximum tri-ester was 4.5 hr. The effect of acid catalyst and temperature led to an increase of tri-ester with an increase in acid catalyst and temperature (Fig. 5b). The impact of time and temperature also resulted in an increase of tri-ester (%) with an increase in the acid catalyst and temperature (Fig. 5c).

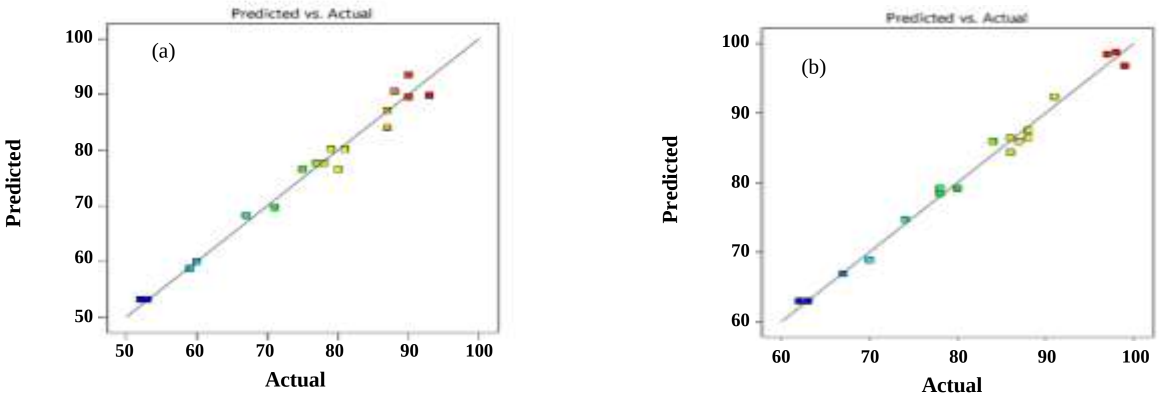
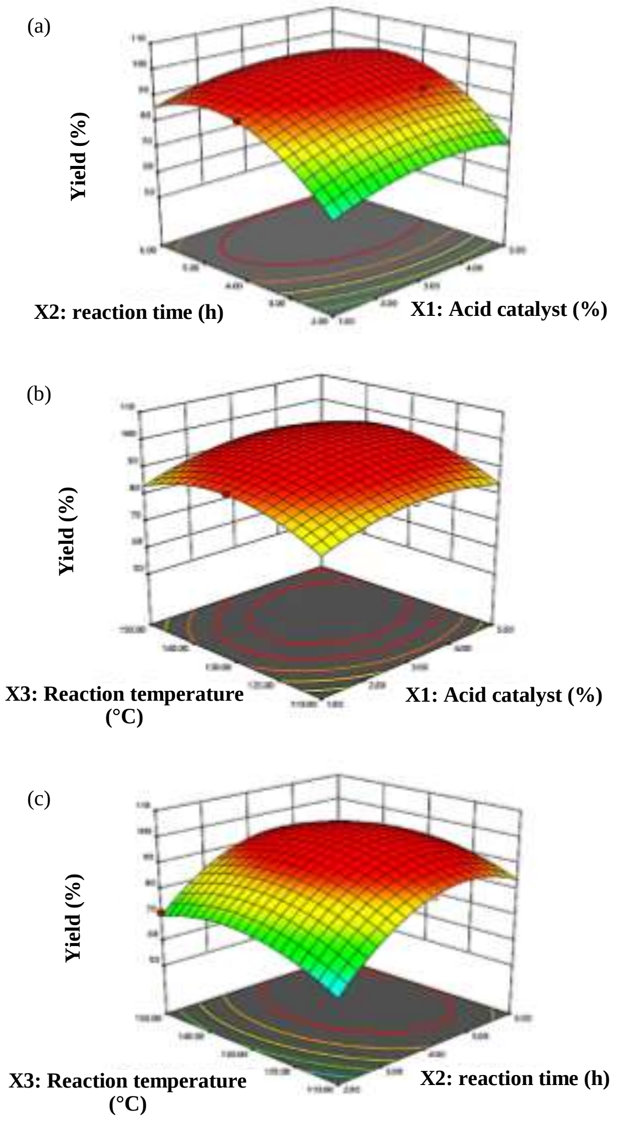


Fig. 3: Regression plot of predicated values versus actual data of (a) yield of ester and (b) tri-ester percentage.



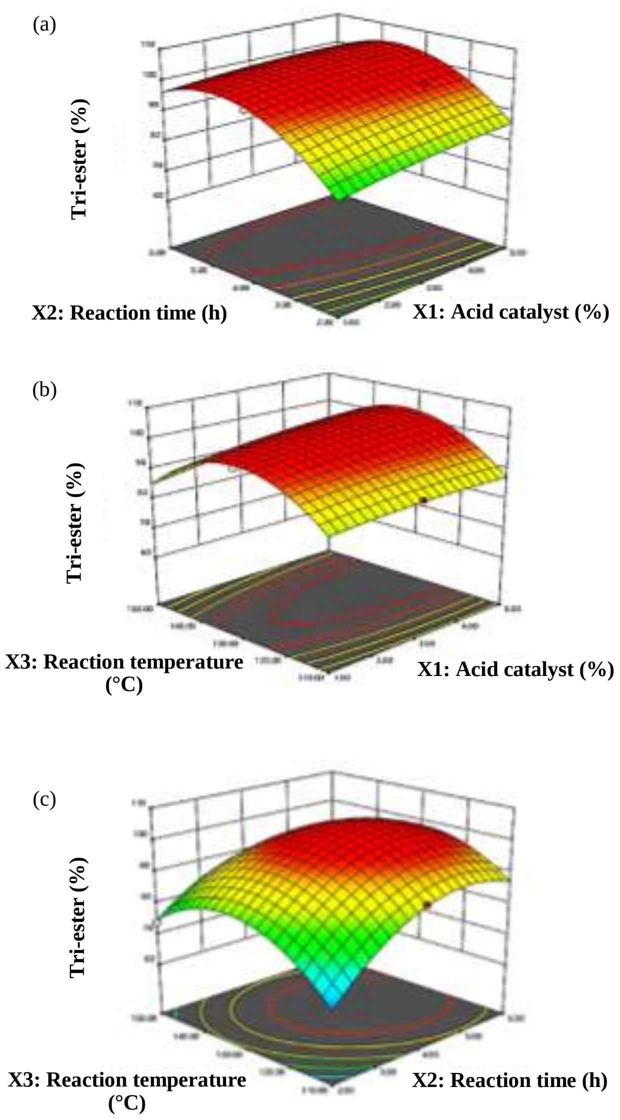


Fig. 4: 3D Response surface plots for the yield (Y_1) as a function of (a) acid catalyst and time, (b) acid catalyst and temperature, (c) time and temperature.

Fig. 5: 3D Response surface plots for the tri-ester percentage (Y_2) as a function of (a) acid catalyst and time, (b) acid catalyst and temperature, (c) time and temperature.

Table 5: Optimization criteria for dependent variables.

Variables	Goal	Lower limits	Upper limits
Acid catalyst (%), X_1	in the range	1	5
Esterification time (hr), X_2	in the range	2	6
Esterification temperature (ºC), X_3	in the range	110	150
Yield (%), Y_1	Maximize	52	93
Tri- ester (%), Y_2	Maximize	62	99

Table 6: Percentage products yields produced by using D-optimal design.

PFAD ester	Y1, % (Predicted)	Y1, % (Actual)	Y1, % (Conventional)
PFAD-TMP	94	93 ± 1.5	89 ± 1.9
PFAD-di-TMP	92	90 ± 2.5	85 ± 2.0
PFAD-PE	90	88 ± 1.6	79 ± 1.3
PFAD-di-PE	87	85 ± 2.0	78 ± 1.7

Model validation and experimental confirmation

The conditions for optimality for the response variables were found, which demands the predicted model be used, so the model was validated using a desirability function. The optimal conditions include the yield of PFAD-TMP ester and a percentage of tri-ester with maximum values, as shown in Table 5 and Fig. 6. The validity of the predicted model was confirmed via a validation test. Meanwhile, optimum conditions were conducted in triplicate, comprising an acid catalyst of 5 (w/v), esterification time of 4.5 hr, and esterification temperature of 150 °C. The final yield was obtained approximately at 93% with 99% selectivity of the tri-esters formation.

At optimal conditions, PFAD-TMP ester was predicted to produce at 93.9% and the study results showed the ester was obtained at the actual yield at 93 ± 1.5 % with 99 % selectivity towards full formation of triesters. The optimal condition was obtained at the condition of 5% cat, 4.5 h reaction time, and 150°C reaction temperature. The same D-optimal optimization technique was also applied for the production of the PFAD other esters. All the optimal processes are following the optimization steps for the PFADS-TMP ester. The results showed that the percent yields (Y_1) of the others esters were slightly lower at their optimal conditions as shown in Table 6. The advantages D-optimal design has greater advantages over the traditional one-variable-at-a-time technique optimization technique as indicated in the table. The D-optimal design offer less time-consuming and do include interactive effects among the variables and response. The advantages of this model have been chosen to optimize multi-discipline works and proved the advantages of the D-optimal design method are shown in Table 7. The methods were good and suitable for work such as building models and multidisciplinary [35], drug delivery [36], milling cutting fluid [37], separation and isolation of fatty acid [38], vegetable oil hydrolysis [39], epoxide ring opening [40], mineralization and discoloration of dye reaction [41], synthesis of plant-based synthetic esters for biolubricants [42], etc.

Structural characterization of PFAD esters

The final products of the synthesized PFAD esters were analyzed using FTIR and NMR (^{1}H, ^{13}C). Mainly FT-IR analysis was used to prove the presence of ester groups. Stretching vibration of the carbonyl group (C=O) for aliphatic esters present in 1733-1740 cm^{-1} wave number range while wave numbers 1690-1725 cm^{-1} represents carboxylic acid (C=O) stretching vibration [43]. From the FT-IR spectra (Refer to Supplementary material 1), the stretching vibration of the carbonyl group (C=O) for aliphatic esters is at the wave numbers 1738, 1740, 1733, and 1740 cm^{-1} for PFAD-TMP, PFAD-Di-TMP, PFAD-PE, and PFAD-Di-PE, respectively. The C-O stretching bands of ester are noticed in the range of 1160 and 1240 cm^{-1}. The range at 3230–3550 cm^{-1} is corresponding

Table 7: The advantages of RSM design methods use for optimization works.

Type of work	RSM optimization design	Advantages	Ref.
Model building and multidisciplinary design optimization	D-Optimal	The method provides a highly efficient approach for approximation model building and for multidisciplinary design	[35]
Drug delivery formulation of self-microemulsion drug delivery system (SMEDDS), PEG200	D-Optimal	Significant interactions among the formulation variables and the desirability function were achieved	[36]
Assessment of vegetable-based cutting fluids for end milling cutting fluid	D-optimal	Appropriate cutting fluid type AISI 304 material was selected in accordance with high efficiency in energy, tool life and surface roughness	[37]
Separation and isolation of palm oleic acid (POA)	D-Optimal	About 86% yield with more than 100% increment in POA liquid fraction	[38]
Vegetable oil hydrolysis	D-Optimal	High 85% yield of free fatty acids was obtained with 98% efficiency	[39]
Epoxide ring opening	D-Optimal	Resulted in 84% yield of hydroxy oil with 0.041% oxirane oxygen content (OOC) with 99% efficiency	[40]
Mineralization and discoloration of dye reaction	D-Optimal	Discoloration rate was high at k_1=0.9447min^{-1} with the highest initial organic load	[41]
Synthesis of plant-based synthetic esters for biolubricants	D-Optimal	A 79% ester yield with 91% selectivity of tetraester CPKO-di-TMPTE	[42]

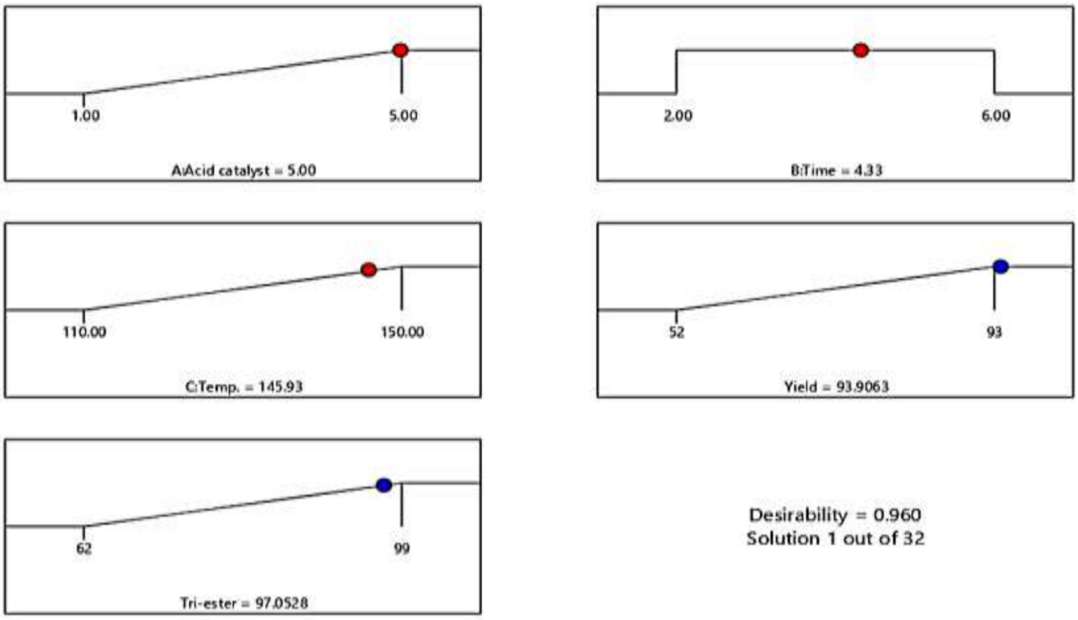


Fig 6: Predicted conditions to produce desirable using D-optimal design.

corresponding to the stretching vibrations of -COOH (carboxylic acid carbonyl) [12]. It can be observed that the signals due to alcohol and acid had disappeared from the final product (ester). Furthermore, a notable peak appeared at 1704 cm^{-1} in the PFAD spectrum, indicating the appearance of the ester carbonyl group indicating the complete esterification of the PFAD.

Moreover, FT-NMR 400 MHz was used to determine the purity and the molecular chemical structure of synthesized esters. The combination of the results from FT-IR with ^{1}H and ^{13}C NMR can prove the success of the esterification reaction. The ^{1}H and ^{13}C NMR spectra of PFAD-TMP ester are indicated by Supplementary materials 2 and 3, respectively.

Table 8: Lubrication properties of PFAD esters.

Esters	Viscosity index (VI)	Pour point (PP) (ºC)	Flash point (FP) (ºC)	Oxidative stability temperature (OST) (ºC)
TMP ester	141±3	5±2	230±3	301±6
Di-TMP ester	148±4	-3±2	245±5	234±2
PE ester	157±3	0±1	235±5	288±4
Di-PE ester	187±5	-5±1	260±8	188±3
Commercial lubricant (PAO6)	132±3	-57±6	226±3	201±5

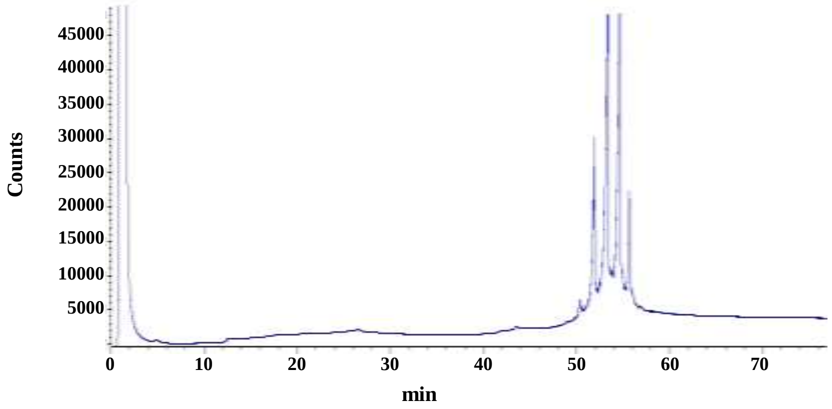


Fig. 7: GC-FID chromatogram of PFAD-TMP ester.

GC-FID analysis

High-temperature column gas chromatogram is important in the determination of tri-ester production in the synthesis of PFAD-TMP ester. The major tri-ester product was observed to be 99% after RSM optimization. The alcoholic –OH functional group of TMP was successfully converted to the ester functional group as the formation of tri-ester peaks starts at 51.20 min (Fig. 7). Tri-ester peaks have been identified according to the carbon number of the alkyl groups attached to the ester-TMP skeleton by following the terminology used in fats and oils analysis [13]. The optimizations by RSM have high efficiency in to opt the optimum condition for the esterification reaction. Where the yield was increased up to 93 ± 1.5% and tri-ester selectivity was increased up to 99 %. This is over the conventional optimization method which gave both values at 89 ± 1.9 and 88%, respectively (Table 6). This study proves that the D-optimal design leveraging the Response Surface Methodology can systematically produce optimal conditions for the synthesis and characterization of PFAD-TMP ester. Additionally, the results reveal that the model can successfully predict the synthesis and characterization of PFAD-TMP ester.

Lubrication properties of PFAD esters

PFAD esters were subjected to specific property tests to ascertain their applicability as biolubricating oil. These properties include oxidative stability (OS), Flash Point (FP), pour point (PP), and viscosity index (VI). The significant lubricating properties of the PFAD esters as a biolubricant are shown in Table 8.

The efficiency of the biolubricant in reducing friction and wear is greatly influenced by its viscosity. Automotive biolubricants must reduce friction between engine components regardless of whether it is being started in a cold climate or running at temperatures of up to 200 °C [44]. The viscosity index (VI) highlights how the biolubricant viscosity changes with the variation in temperature [45]. A low VI represents relatively large changes in kinematic viscosity induced by changes in temperature. On the other hand, a high VI indicates that kinematic viscosity is largely constant over a wide temperature range [46]. An engine is better off using biolubricants with a high VI, as even when the engine is cold, the biolubricant will not thicken excessively, and engine start and circulation will be fast [47]. As the synthesized PFAD esters have shown high VI values in the range of 141± 3 to 187± 5, they can be classified as high VI fluids base esters. In general, the VI values of the PFAD esters are higher than commercial lubricants (PAO6) whose VI of 132±3 (Table 8).

The Pour Point (PP) is the minimum temperature at which the biolubricant oil will pour or flow when it is cooled. The PP should be low enough to ensure that the biolubricant is pumpable when the equipment is initiated at extremely low temperatures. According to *Cecilia et al.* (2020) [6], industries are now using very low PP esters to formulate greases, such as gear oils, compressor oils, marine engine oils, and hydraulic fluids. Because branched esters have excellent flow characteristics at low operating temperatures, they particularly blend well in automotive engine oil applications. The PP of PFAD esters was measured by ASTM D-97 and is summarized in Table 8. In this work, the ester-TMP, ester-Di-TMP, ester-PE, and ester-Di-PE, have PP of 5, −3, 0, and -5 °C, respectively. The PFAD Di-PE ester has a high degree of branching which significantly decreased its PP. *Totten et al.* (2003) [48] stated that increasing branching at a constant carbon chain number will decrease the PP of the ester. *Cermak et al.*, (2006) [49] found that linear carbon chained esters have higher PP compared to branched esters. This is because crystallization is prevented by a steric barrier around the individual molecule, owing to the presence of a large branching point in the PFAD esters, thus decreasing its PP.

Flash Point (FP) is the lowest temperature at which a biolubricant will form a vapor in the air near its surface that will briefly ignite, on exposure to an open flame. The FP should be high to allow safe operation and minimum volatilization upon maximum operating temperature [50]. It is also easy to select the temperature for storing the biolubricant, and which transportation type to use if the FP of the oil is known. At the highest operating temperature, the biolubricant should be minimally volatile and safe enough to operate, and therefore must have a sufficiently high FP [46]. PFAD ester FP is shown in Table 8. It was known from this study that the values of FP increase with molecular weight. Di-PE ester (793.1 g/mole) and Di-TMP ester (789.2 g/mole) have the highest FP value at 260±8 and 245±5°C, respectively, among other PFAD esters. While TMP-ester (673 g/mole) and PE-ester (675 g/mole) have FP of 230±3 and 235 ±5 °C, respectively. The high FP of PFAD-esters makes it suitable to be used for aviation jet engines [38]. Esters become combustible above FP of 43 °C, and flammable below this temperature [39]. A commercial lubricant (PAO6) has FP of 226±3 °C and all the prepared esters have a higher FP than the PAO6. The esters still maintained good lubrication even at high temperatures.

Another important property of biolubricant is oxidative stability, which determines the degree of resistance of the biolubricant to oxidative degradation. Biolubricant oil must have a really long lifespan, especially if it were to be used in heat transfer units, transformers, turbines, and hydraulics. The esters that have potentially been used as biolubricants must not oxidize too fast, the rate of which depends on their hydrocarbon chain chemical composition [40]. *Encinar et al.* (2020) [50] explain that the more stable the biolubricant, the higher its Oxidative Stability Temperature (OST) value. The OST of PFAD esters is presented in Table 8. A rather unexpected outcome was discovered, when TMP-ester and PE-ester emerged with the highest OST values among others were 301±6 and 288±4 °C, respectively. While, OST values of Di-TMP ester and Di-PE esters were 234±2 and 188±3 °C, respectively. Several possible factors could be found from its low branching and uniform structure or may be due to the trans-configuration of its branching, which is thermodynamically more stable than the cis form [34]. Despite having a more carbon-hydrogen bond with higher molecular weight, the OST value of Di-PE ester is insignificant compared to other PFAD esters. This finding is somewhat counterintuitive and might be due to a negative effect from the increase of branching in Di-PE ester against the OST value [40]. *Bahadi et al.* (2019) [51] supported this finding by claiming that the OST decreases with the increase of branching in the ester. In general, all PFAD esters showed high OST values in the range of 188-301 °C, which would indicate their suitability to be used as a commercial lubricant without any antioxidant additives.

CONCLUSIONS

The D-optimal design has successfully shown the independent variables' interaction and its effect on the PFAD-TMP ester esterification. The findings validate the model predictions for the esterification of PFAD and polyhydric alcohol, TMP. The optimization for PFAD-TMP-ester production was the best fit with the highest yields and selectivity compared to other esters of PFAD-Di-TMP, PFAD-PE, and PFAD-Di-PE. The enhanced esterification reaction might be due to less steric hindrance to the low-branched hydrocarbon chain of TMP as compared to the high-branched of other PFAD esters. The results indicate that the PFAD esters produced have good lubrication properties with acceptable PP, high OS, FP, and VI respectively. High lubrication properties may due to the unique chemical structure of PFAD esters. Besides having a high-branched hydrogen chain, the esters have a high molecular weight that contributes to good lubrication properties. The PFAD-based ester produced indicate acceptable and good lubricants that can be used in various industrial application, especially in warm climates countries.

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