Journal of Sustainable Energy & Environment

12 (2021) 35-44

Journal of
Sustainable
Energy &
Environment

Biolubricant synthesis by esterification of palm fatty acid

Papon Srisanong, Pornlada Daorattanachai, and Navadol Laosiripojana*

The Joint Graduate School of Energy and Environment, Center of Excellence on Energy Technology and Environment, King Mongkut's University of Technology Thonburi, 126 Pracha Uthit Rd., Bang Mod, Thung Khru, Bangkok 10140, Thailand
*Corresponding author: navadol.lao@kmutt.ac.th

Abstract: This work is focusing on producing synthetic ester based biolubricant from cheap and non-edible source, i.e., palm fatty acid distillate (PFAD), as a substrate. Biolubricant was synthesized by esterification reaction with polyhydric alcohol, i.e., trimethylolpropane (TMP), in order to produce polyol ester (triester) which has more thermal stability than monoester and diester. With concerns of using high corrosive Brønsted acid as a homogeneous catalyst, the novelty of this study is the use of methane sulfonic acid (MSA) in the transformation of PFAD to TMP-based triester as a biolubricant. This research studied and optimized the effect of production variables including temperature, time, catalyst loading and molar ratio by applying the response surface methodology (RSM) based on central composite design (CCD) of experiment. The reaction condition of 160 ℃, 6 h, catalyst loading 1.5% by weight of PFAD and 3:1.5 PFAD:TMP molar ratio with a percentage conversion of 99.65% and 32.26% oleic triester yield was selected as a center point for optimization. The optimized condition obtained from the statistical software was 160.7 ℃, 4 h, catalyst loading of 1% by weight of PFAD and 3:1.99 with oleic triester yield 38.17%. Finally, the lubrication properties of the product were compared with other works. In this study, it was found that the viscosity index, pour point, oxidation induction time, and wear scar diameter (WSD) of synthetic biolubricant were 126, 12 ℃, 130 ℃ for 12 min, and 0.62 mm, respectively.

Keywords: Synthetic lubricant, Palm fatty acid, Esterification, Methane sulfonic acid.

1. Introduction

The term "Biolubricant" is all lubricants that are both rapidly biodegradable and non-toxic to humans and aquatic environment [1]. Biolubricant can be vegetable oil based or synthetic ester that fabricated from renewable oil or mineral oil based. Comparing with mineral oil, many works have indicated that, vegetable oil possess better lubricity, anti-corrosion, and better viscosity-temperature characteristics. Moreover, vegetable oils are readily biodegradable and environmentally safe compared to mineral oils [2-3]. These suggestions are driven by the fact that vegetable oils are basically complex of triglycerides of fatty acids with carbon chain ranging from C12-C22 atoms which might have 0-3 double bond in their hydrocarbon chain. Triglyceride of vegetable oils are known to provide an excellent lubricity due to mild polarity of triacylglycerol can attach to the metal surface while allowing the non-polar fatty acid chain forming a monolayer film provides a desirable quality of boundary lubrication [2]. In addition, the intermolecular interaction in fatty acid side benefits in viscosity stability and ignition temperature as well. However, until these days biolubricants still not being widely used because of limitations in their performance and production challenges. Major drawbacks of vegetable oil based biolubricants, as reviewed by some researched works, are usually have low thermal oxidative stability, poor cold flow behavior and hydrolytic stability [2, 4-6]. These issues are due to the degree of unsaturation of the vegetable oil and natural weak spot on beta hydrogen in triacylglycerol molecule. Therefore, these drawbacks are directly affected to the lubrication performance (tribological performance) of biolubricants. Commercial biolubricants can be divided into 3 types i.e., synthetic ester, synthetic fatty acid and hydrocarbon [5]. While the most commercially marketed biolubricant is a synthetic ester due to possibilities to produce many types of esters for wide range of applications and better lubrication quality than vegetable oil. Polyol ester-based lubricants, especially trimethylolpropane ester, are attractive as they tend to have better thermal stability than diester [5, 7]. Synthetic esters can be produced by couple of pathways i.e., transesterification and esterification. Mostly, research on transesterification of vegetable oil triglycerides is more attention in developing the alkali heterogeneous catalyst over the strong acidic homogeneous catalyst due to the corrosion and product normalization difficulties [7-8]. While research on esterification of vegetable oil fatty acid is focusing on enzymic catalytic reaction, where the major drawback is a very long reaction time, instead of acidic catalyzed [9]. Nevertheless, for both approaches on synthetic ester production, many research papers did not ensure to make food vs fuel argument a non-issue.

There is a possibility to produce a biodiesel, ester-based product as biolubricant, by non-edible sources e.g., waste cooking oil, jatropha cake oil, grease oil, waste animal fats and palm fatty acid distillate (PFAD) [10]. In this case, PFAD has a high potential to be studied as a feedstock for polyol ester based biolubricant production via esterification. The physicochemical of the palm fatty acid consists of more than 90% free fatty acid content which includes palmitic acid and oleic acid as a dominant component [11]. While other component e.g., linoleic, stearic and myristic acid are share very small portion [11]. This physicochemical result palm fatty acid indicates that high free fatty acid value is suitable for esterification with strong acid catalyst [10]. However, drawbacks of strong homogeneous acid catalyst, e.g., sulfuric acid, are mainly high degree of corrosive, product normalization and separation. Therefore, it is proposed of using methane sulfonic acid (MSA) as it possesses high acid strength, considered to be biodegradable, less corrosive and toxic than other mineral acids [12].

Therefore, this research aims to produce TMP-based triester from PFAD in a presence of MSA at different temperature, catalyst loading and reactants molar ratio. Its lubrication properties would be characterized in order to identify product quality compared to other published works.

2. Methods and Materials

2.1 Materials

In this study 97% Trimethylolpropane (TMP) was purchased from Aldrich chemistry (Germany) while palm fatty acid distillate (PFAD) was received from Pathum oil company (Thailand). Aldrich chemistry (Germany) also supplied 99% methane sulfonic acid (MSA), 90% oleic acid, stearic acid and palmitic acid. In addition, potassium hydroxide, hydrochloric acid, n-hexane and tetrahydrofuran also used in this study.

2.2 Characterization of Palm Fatty Acid Distillate (PFAD) and reaction product

2.2.1 Saponification value (SV) of PFAD

In this study, PFAD was used as a biolubricant feedstock. The physical and chemical properties of the PFAD were determined and then compared with another related research. As provided by American Oil Chemists' Society standard, AOCS official method cd 3-25, the definition of a saponification value is the amount of alkali necessary to saponify a definite quantity of the fatty acid in the sample [11]. The saponification value is expressed as a number of milligrams of Potassium Hydroxide (KOH) required to saponify one gram of the test sample. In addition, saponification value can also be used to determine the average molecular weight of free fatty acids in the PFAD [11, 13].

2.2.2 Fatty acid and chemical composition of PFAD and reaction product

The fatty acid and chemical composition of PFAD and reaction product were determined using gas chromatography-mass spectrometry (GC-MS 2010 Plus Shimadzu). The GC-MS was equipped with a capillary column DB-5 (30 m × 0.25 mm × 0.25 μm). The PFAD was prepared by dissolved in Tetrahydrofuran solvent (THF) with the concentration of 25 mg/ml and then transferred into the 2 ml vial. 1 μl of sample was injected into the GC-MS with column oven and injection temperature 150°C hold for 5 min then raised to 240 °C with a rate 5 °C/min after that hold for 10 min and finally raised to 300 °C with a rate 10 °C/min and hold for 2 min. Select split injection mode and Helium flow in column 1 ml/min. While the MS ion source and interface temperature were both 200 °C. The fatty acid and chemical composition of the PFAD and reaction product were obtained by the relative percentage of total peak area and the identity of each peak was matched with the library database.

After successfully identify the main composition of fatty acid in PFAD and reaction product, the quantitative analysis could be done by using gas chromatography equipped with flame ionization detector (GC-2010 Shimadzu). The analysis was performed using the same column specification as in GC-MS. The oven temperature was initially set at 150 °C, held for 3 minutes, then increased to 300 °C at the rate of 10°C/min and held for 20 minutes. The injector and detector temperature were set at 250 °C and 300 °C, respectively. Linear velocity was selected for the carrier gas flow mode with the column and purge flow at 2 ml/min and 3 ml/min, respectively. Finally, the split ratio was set at 50:1 and 1 μl of sample was injected to the GC system.

After the fatty acid composition in PFAD was determined by GC-MS, the standard calibration curve of each fatty acid was made. So, the percentage by weight of each fatty acid including approximated molecular weight of PFAD could be determined using GC-FID. In this study the standard fatty acid including palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1)

The esterification between fatty acid and TMP can produce three group of esters, namely, monoester (ME), diester (DE), triester (TE) and water a by-product [14]. But, since the standard for TMP-based ME, DE and TE were not available commercially. In this study the TE percentage yield of different reaction conditions were calculated by assuming the percentage peak area of TE to the total product was directly proportional to the amount of TE formed. In addition, in this study the percentage yield of TE on different reaction conditions were considered only TE that was converted from oleic acid.

2.3 Design of experiment

2.3.1 Equipment set up

The esterification reaction of PFAD and TMP in a presence of MSA catalyst was conducted in a 100 ml screw cap glass test tube which placed in a temperature-controlled oil bath. After loading reactants, the glass test tube was sealed with silicone stopper and all esterification reactions were performed under a continuous flow of Nitrogen gas. The purpose of using continuous flow of inert Nitrogen is to mitigate the degradation of unsaturated oils and fats due to an autoxidation chain reaction that occurs in the presence of oxygen [15]. The esterification reaction started by loading 14.5 g PFAD with the stoichiometric amount of TMP into 100 ml screw cap test tube. Then enclosed the tube by silicone stopper and connected both inlet-outlet nitrogen hose. Purged the nitrogen around 3 minutes and then heated up the mixture to the desired temperature. After the temperature was steady, the calculated amount of 10% MSA was injected to the reactant mixture and time was recorded.

2.3.2 Statistical analysis and design of experiment

- Screening test

Screening test was conducted in order to study the effect of each factor to responses. The screening test cannot be used examine the interaction between variables, but it requires less runs of experiment rather than general full factorial design [16]. In this case four effects i.e., reaction temperature, reactant molar ratio, catalyst loading based on weight of PFAD (10% concentration MSA) and reaction time were studied. As shown in Table 1 there are 20 runs for screening each effect interacts to responses. The screening process started with the lowest level of all effect then increase the level of each effect. These 20 samples were then analyzed with GC-FID in order to determine the percentage reaction conversion.

- Reaction condition optimization

From the screening test, the level that gives the optimum response for each effect was used as a center point for the response surface methodology (RSM). In this study, RSM based on central composite design (CCD) of experiment. Both of experimental design and data analysis were performed in Design Expert 10 (Stat-Ease Inc., Minneapolis, MN, USA). Benefits of applying CCD are able to estimate first-order and second-order terms and model the response variable with curvature (quadratic equation) which requires smaller number of experiments compare to general full factorial design [17].

There were two responses to be investigated i.e., percentage reaction conversion (Y_1) and the percentage yield of TMPTE (Y_2). These two responses were investigated as a result of varying reaction temperature (°C) (X_1), reactant molar ratio (X_2), catalyst loading (% weight of PFAD) (X_3) and reaction time (hour) (X_4). With 2 center points and alpha value of 2, the CCD was executed for 26 runs as shown in Table 2. Then experimental results were used as a basis for proposing a mathematical model that supported by the analysis of variance (ANOVA). Finally, checking the competency of the model by the diagnostic plots.

2.4 Catalyst comparison

The capability 10% MSA as a catalyst was compare with esterification in presence of sulfuric acid, heterogeneous catalyst and without catalyst. The amount of proton dissociated in the esterification reaction when using 10% MSA was calculated, and the equivalent amount of sulfuric acid was added to the reaction

Table 1. Levels of each independent variable and the number of total runs for study an interaction of each effect to responses.

Effect	Condition				
(X_1) Temperature (℃)	120	140	160	180	200
(X_2) Reaction Time	2	4	6	8	10
(X_3) Catalyst loading (% weight of PFAD)	0.3	0.5	1	1.5	2
(X_4) Molar ratio (PFAD:TMP)	3:1	3:1.5	3:2	3:2.5	1:1
Total screening run	20				

Table 2. Experimental runs from central composite design.

Run	X1	X2	X3	X4	Y1	Y2
1	140	8	2	1	91.16	27.05
2	140	8	2	2	99.81	34.04
3	160	2	1.5	1.5	99.12	32.09
4	120	6	1.5	1.5	99.52	32.37
5	140	8	1	1	94.76	26.29
6	180	4	2	2	99.47	34.33
7	180	8	1	2	99.56	36.56
8	160	6	1.5	2.5	99.89	40.65
9	180	4	1	2	99.65	39.09
10	180	8	1	1	96.14	28.83
11	160	10	1.5	1.5	99.38	33.29
12	180	4	1	1	96.53	31.39
13	140	8	1	2	99.79	36.80
14	180	4	2	1	99.48	30.99
15	160	6	1.5	1.5	99.65	32.26
16	160	6	2.5	1.5	99.63	31.94
17	180	8	2	1	98.88	29.29
18	140	4	2	2	99.56	34.07
19	200	6	1.5	1.5	97.90	33.43
20	140	4	2	1	99.37	27.28
21	160	6	1.5	0.5	90.00	25.00
22	180	8	2	2	98.18	34.57
23	140	4	1	2	99.51	37.45
24	160	6	1.5	1.5	98.44	33.06
25	140	4	1	1	93.56	27.66
26	160	6	0.5	1.5	98.98	34.48

In this case the condition for esterification was 160 ℃, 6 h and 3:1.5 PFAD:TMP (center point condition).

2.5 Lubrication characteristic

The lubrication property of the final product was tested by four properties; kinematic viscosity, pour point measurement, oxidation stability and anti-wear property. In order to prepare the sample, the esterification reaction was scaled-up from laboratory glassware to 2 L bench top reactor (Parr Instrument Company, Series 4520). While the center point reaction condition was set for the esterification reaction. After finishing the reaction, product was washed with deionized water (DI) so the excess TMP as well as the MSA catalyst were separated with esters.

2.5.1 Kinematic viscosity test

Kinematic viscosity is defined as the ratio of the viscosity to the density of the fluid. Kinematic viscosity measurement was carried out according to ASTM D445-19 standard method at 40℃ and 100℃. In addition, the viscosity index for the product ester was calculated according to the standard method ASTM D2270-93 [18-19].

2.5.2 Pour point measurement

The pour point of liquid is the temperature below which liquid is unable to flow. Pour point measurements of product esters was performed according to standard method ASTM D5950-14 [18-19].

2.5.3 The oxidation stability of the product

Measuring the oxidative stability or the resistance of a product ester to oxidative decomposition. The oxidative stability analysis was carried out according to ASTM D6186-19 using pressure differential scanning calorimetry (PDSC) technique. By calorimetric measurement of the time interval to the beginning of the exothermal oxidation of the material, which is exposed to an oxygen or air atmosphere under atmospheric pressure at a fixed temperature [18, 20].

2.5.4 Anti-wear properties test

The purpose of this test is to determine the wear preventive characteristics of a lubricant. The anti-wear properties for the product ester were evaluated according to ASTM 4172-18 or a four-ball test method. The test is going to be conducted using a four-ball tester. Four-ball wear test, a steel ball is rotated against three lubricated stationary steel balls under a specified load, speed, temperature, and time [19].

3. Results and Discussion

3.1 PFAD characteristic

In this study, the PFAD sample was pale yellow solid at room temperature. The mean SV of PFAD sample was found to be in range between 241.62 ± 5.93 mgKOH/g which was lower than other study [11] as shown in Table 3. Table 4 shows fatty acid composition in PFAD sample as a percentage by weight. In this case, fatty acids were including palmitic acid (C16:0), stearic acid (C18:0) and oleic acid (C18:1) which approximately contain 49.42%, 4% and 46.58% by weight of PFAD, respectively. From this result, the molecular weight of PFAD used in this study could be approximated, which was calculated to be 269 g/mol.

3.2 Screening test

3.2.1 Effect of temperature

The effect of reaction temperature was studied at fixed reaction time, 10% MSA loading and reactant molar ratio at 2 h, 1.5% of PFAD weight and 3:1 PFAD:TMP. Due to the result shown in Figure 2A, reaction temperature significantly impacted on the reaction conversion. The percentage reaction conversion at the reaction temperatures 120 ℃, 140 ℃, 160 ℃, 180 ℃ and 200 ℃ were 47.62%, 90.06%, 92.83%, 94.65% and 94.93%, respectively. The reaction conversion was below 50% at the reaction temperature equal to 120 ℃ then abruptly increase to more than 90% when the reaction temperature got higher than 140℃. Moreover, in this case, the reaction was operated in an enclosed 100 ml test tube with a continuous flow of nitrogen gas which by product water has a possibility to evaporate more at higher temperature. Therefore, the esterification shifted forward and consequently, higher reaction conversion. For this effect, reaction temperature of 160 ℃ was selected to be an optimum level.

3.2.2 Effect of reaction time

The effect of reaction time was studied at fixed reaction temperature, 10% MSA loading and reactant molar ratio at 120 ℃, 1.5% of PFAD weight and 3:1 PFAD:TMP. The percentage reaction conversion at the reaction time of 2 h, 4 h, 6 h, 8 h and 10 h were 47.62%, 52.41%, 91.29%, 92.87% and 90.68% as shown in Figure 2B. From this result the reaction conversion was significantly change from about 50% up to more than 90% when the reaction time was more than 6 hrs. However, for the reaction time of 10 h, the reaction conversion was drop from 92.87% at 8 h to 90.68%. This finding was similar to the previous research works which explained that the continuous occurring reverse reaction might associate to the breaking down of TE DE and ME back to fatty acid [1, 18]. While the breaking down of esters might occurred due to the presence of water as a byproduct, that did not remove by nitrogen purge flow, hydrolyzed TE to DE, ME and back to fatty acid. Therefore, at longer reaction time there is more possibility of ester product can convert back to reactants causing the lower reaction conversion. For this effect, reaction time of 6 h was selected to be an optimum level.

3.2.3 Effect of catalyst loading

In this study, 10% MSA was used as a reaction catalyst rather than concentrated MSA. Because the concentrated MSA induced a dark appearance to the end product which some researchers indicated as a side reaction i.e., auto-oxidation reaction [9]. The effect of catalyst loading was studied at fixed reaction temperature, time and reactant molar ratio at 120 ℃, 2 h and 3:1 PFAD:TMP. As shown in Figure 2C the percentage reaction conversion of 10% MSA as a catalyst loading based on PFAD weight of 0.5%, 1%, 1.5%, 2% were 10.51%, 33.62%, 47.62% and 48.11%, respectively. While the catalyst loading at 2.5% by weight of PFAD weight the product was became solid at room temperature in short time after the reaction was finished. In this case the final product that collected after the reaction, appeared to have solid and liquid phase mixing when it was get cooled down to the room temperature. According to previous research that palm oil-based trimethylolpropane triester (TMPTE) has a low pour point at 5 ℃ [1]. So, the TE product from esterification reaction between PFAD and TMP should be in liquid phase at room temperature. In order to, analysis the reaction conversion by GC-FID, the solid phase must be separated from the liquid phase. For this effect, 10% MSA catalyst loading 1.5% by weight of PFAD was selected as an optimum level.

Table 3. PFAD characteristic of this study compared to other studies.

Parameter	This study	[13]				
	PFAD	PFAD-1	PFAD-2	PFAD-3	PFAD-4	PFAD-5
Physical appearance at room temperature	Pale yellow solid	Reddish brown semi solid				
SV (mgKOH/g)	241.62 ± 5.93	209.70±2.50	203.60±8.66	200.39±6.68	195.23±5.68	219.64±6.44

SV = saponification value

Table 4. Percentage of fatty acid composition in PFAD as a percentage by weight.

Fatty acid	Percentage weight in PFAD
Palmitic acid; C 16:0	49.42
Stearic acid; C 18:0	4.00
Oleic acid; C 18:1	46.58

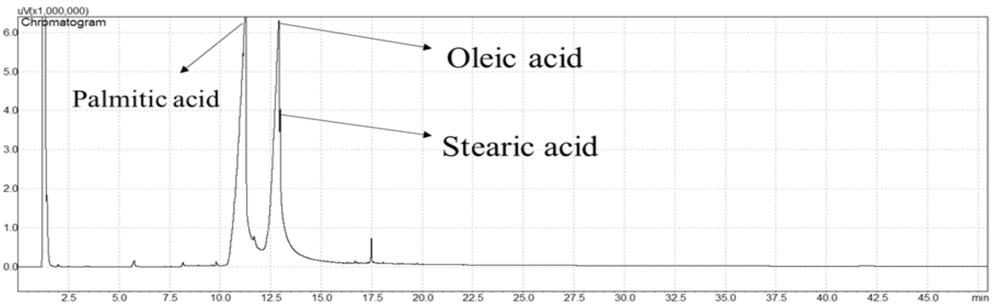

Figure 1. GC-FID chromatogram of PFAD raw material.

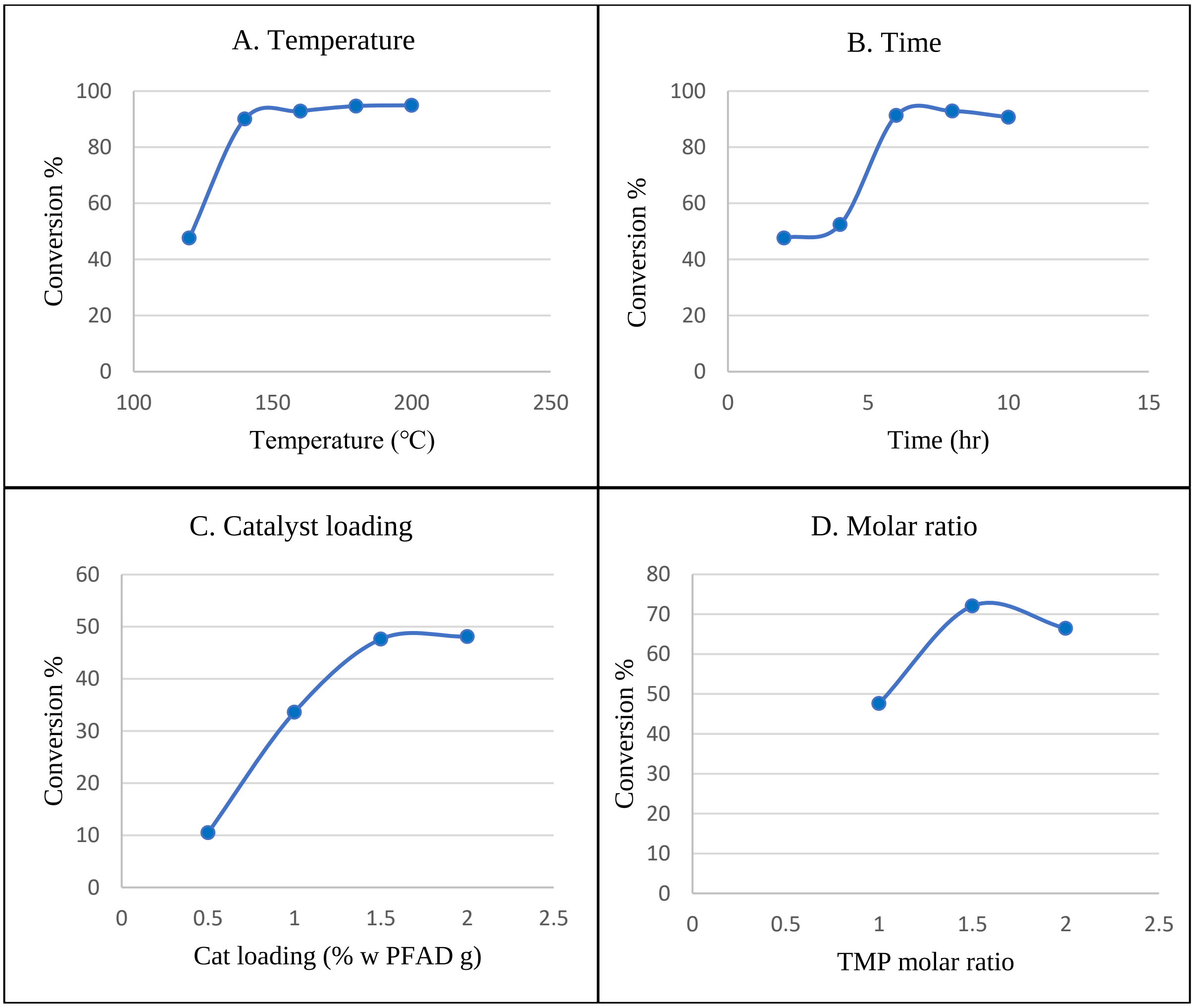

Figure 2. (A) Effect of temperature (B) Effect of reaction time (C) Effect of 10% MSA loading and (D) Effect of reactant molar ratio on esterification of PFAD-TMP.

3.2.4 Effect of reactant molar ratio

The effect of reactant molar ratio was studied at fixed reaction temperature, time, and 10% MSA loading at 120℃, 2 h and 1.5% of PFAD weight. The percentage reaction conversion at reactant molar ratio (PFAD:TMP) of 3:1, 3:1.5 and 3:2 was 47.62%, 72.06% and 66.45%. While reactant molar ration of 3:2.5 and 1:1 the product became solid at room temperature. With similar situation as the effect of catalyst that the final product had two phases mixed, so the separation of the solid phase must be done. A higher percentage reaction conversion was obtained when there was an excess of TMP from the correctly stoichiometric ratio of 3:1 to 3:1.5. However, at higher level of TMP excess to the reaction the percentage conversion was drop as can be seen at reactant molar ration of 3:2 and the final product became solid phase at 3:2.5 and 1:1. This might be the more excess TMP, the more trimethylolpropane monoester (TMPME) and trimethylolpropane diester (TMPDE) would form rather than TMPTE. Moreover, ME and DE were able to be hydrolyzed back to fatty acid due to the reversible mechanism of esterification reaction. In addition, TMP was solid polyhydric alcohol at the room temperature which an unreacted TMP might promoted the product to become solid. Figure 2 (A) Effect of temperature (B) Effect of reaction time (C) Effect of 10% MSA loading and (D) Effect of reactant molar ratio on esterification of PFAD-TMP.

At this point the optimum level of each effect i.e., reaction temperature 160℃, reaction time 6 hr, 10% MSA catalyst loading 1.5% by weight of PFAD and PFAD:TMP ratio of 3:1.5 were selected as a center point for optimization analysis and as a reaction condition for catalyst comparison and lubrication properties analysis of the end product.

3.3 Esterification with fatty acid standards

Since the standard for TMP-based ME, DE and TE were not available commercially. Additionally, there was an attempt to determine the percentage yield of TE by synthesize the TMP-based TE from esterification between palmitic acid standard and oleic acid standard with TMP under reaction condition of 160℃, 6 h, 10% MSA catalyst loading 1.5% by weight of PFAD and fatty acid: TMP ratio of 3:1.5. The chemical composition and identification of chromatogram peaks of end product from palmitic acid and oleic acid were analyzed by GC-MS and GC-FID, respectively. According to GC-MS chromatogram, Figure 3, of the product from esterification with palmitic acid standard, only diester was matched with the mass-spectroscopy (MS) library database. While product from esterification with oleic acid standard, triester was detected. Although, the detected triester was not TMP-based (rather it was glycerol-based triolein $C_{57}H_{104}O_6$) but its structure and molecular weight was similar. So, the peak that lied at the same position of triolein, was assumed to be a desired product (TMP-based triester from oleic acid). Hence, the qualitative analysis, i.e., percentage yield, could be estimated based on triester of oleic acid.

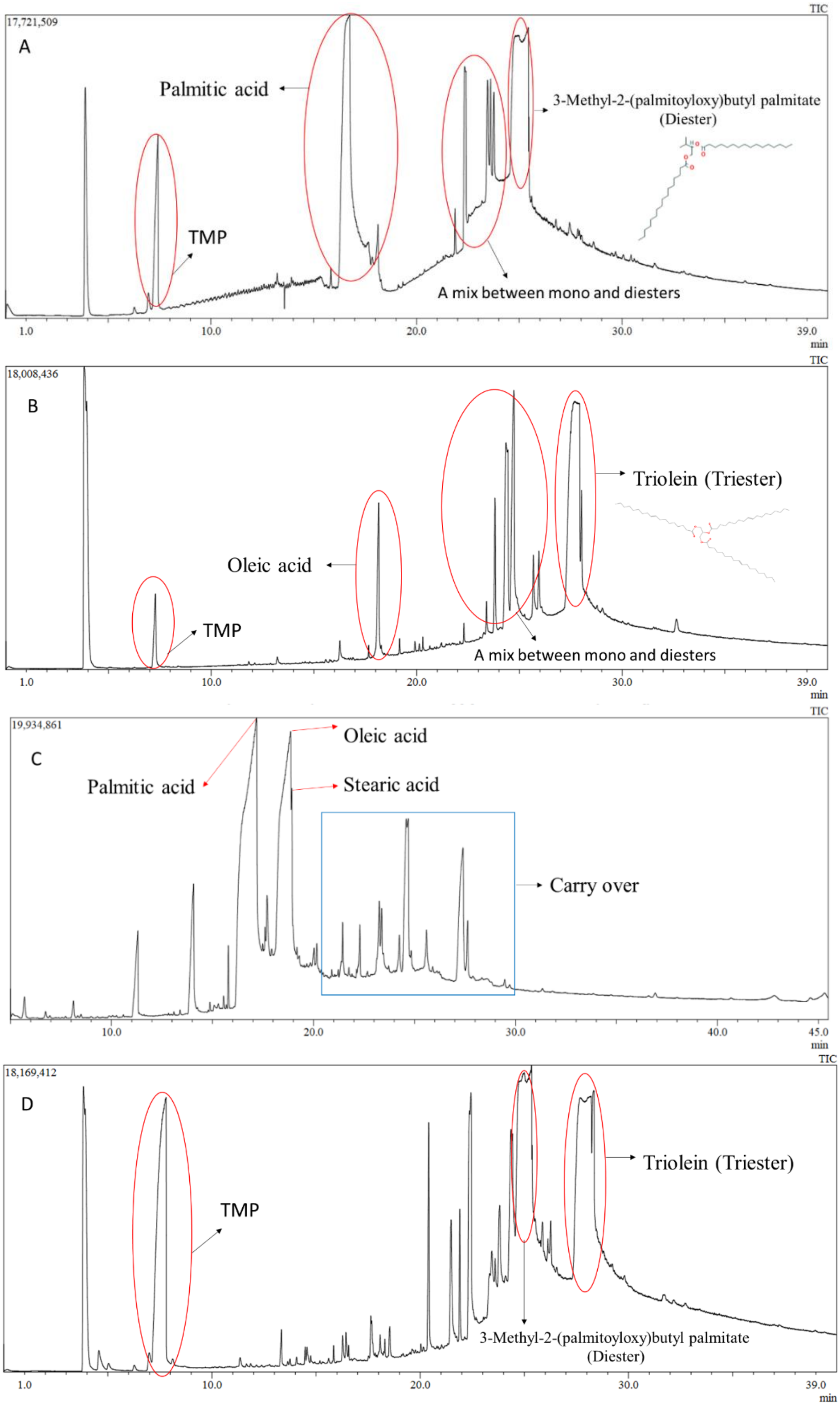

Figure 3 GC-MS chromatogram of (A) End product of reaction with palmitic acid standard (B) End product of reaction with oleic acid standard (C) PFAD raw material (D) End product of reaction with PFAD.

3.4 Catalyst comparison

There were three experiments using different catalyst i.e., 10% MSA, sulfuric acid and esterification with no presence of catalyst. Under the identical reaction condition, the result was shown in Table 3. At the equivalent H^+ amount, the percentage conversion of esterification in presence 10% MSA and sulfuric acid were 99.65% and 99.07%. While the esterification with no catalyst has percentage conversion of 94.31%. These results suggested that the esterification between PFAD and TMP could occur with high percentage conversation with this reaction condition. While catalyst helped the reaction conversion to become higher. However, only the reaction with 10% MSA and no catalyst were able to determine the percentage yield of oleic triester. Because there were no peak appeared at the point of oleic triester from the product of esterification reaction with sulfuric acid and heterogeneous catalyst as shown in Figure 4 A-E. Though, the percentage yield of oleic triester from esterification with 10% MSA and no catalyst were 32.26% and 12.99%, respectively. This suggested that 10% MSA promote the reaction conversion as well as the yield.

3.5 Lubrication properties of end product

Lubrication properties of end product including kinematic viscosity, pour point measurement, oxidation stability and anti-wear property were evaluated and compared with previous research. The TMP-based triester synthesized from palm kernel oil by other work was reported to have high yield of 85.26% so their tested lubrication properties were suitable to set as a benchmark for this study [18].

Table 5. Percentage reaction conversion and percentage yield of oleic triester of esterification with different catalyst.

Type of catalyst	Percentage reaction conversion	Percentage yield of oleic TE
10 % MSA	99.65	32.26
Sulfuric acid (H_2SO_4)	99.07	n/a
No catalyst	94.31	12.99

n/a = Not available

Polyol ester that synthesized palm oil mill effluent (POME) polyol ester via transesterification with TMP was also compared [20]. Additionally, the lubrication properties of commercial biolubricant based on 2-ethylhexyl ester of dimer fatty acid was also compared. As shown in Table 6, the viscosity index of the end product was 126, which lower than palm kernel TMP triester and commercial biolubricant Radialube 7121. This indicated that the end product has more variation in viscosity over a wide range of temperature. Pour point indicate the temperature at lubricant lost its fluidity. The end product was significantly having lower pour point than TMP triester, POME polyol ester and Radialube 7121, i.e., 12 °C, -10 °C, 5°C and -33 °C. This might be caused by the low percentage yield of TMPTE and the presence of saturated fatty acid chain, i.e., palmitic acid, effecting to the higher pour point [21]. The oxidation stability of lubricant can be reported with different ASTM standard but in this study ASTM D6186-19 the oxidation induction time (OIT) for lubricating oil was used. The OIT of the end product was 2 min at 130 °C which lower than POME polyol ester of 45 min at 150 °C. This indicated that the end product form this study was susceptible to be oxidized which might be due to high level of unsaturated fatty acid chain presence in the product. The four-ball wear test indicated the anti-wear property of the lubricant by measuring a wear scar diameter (WSD). With a smaller WSD, a better ability to reduce friction and

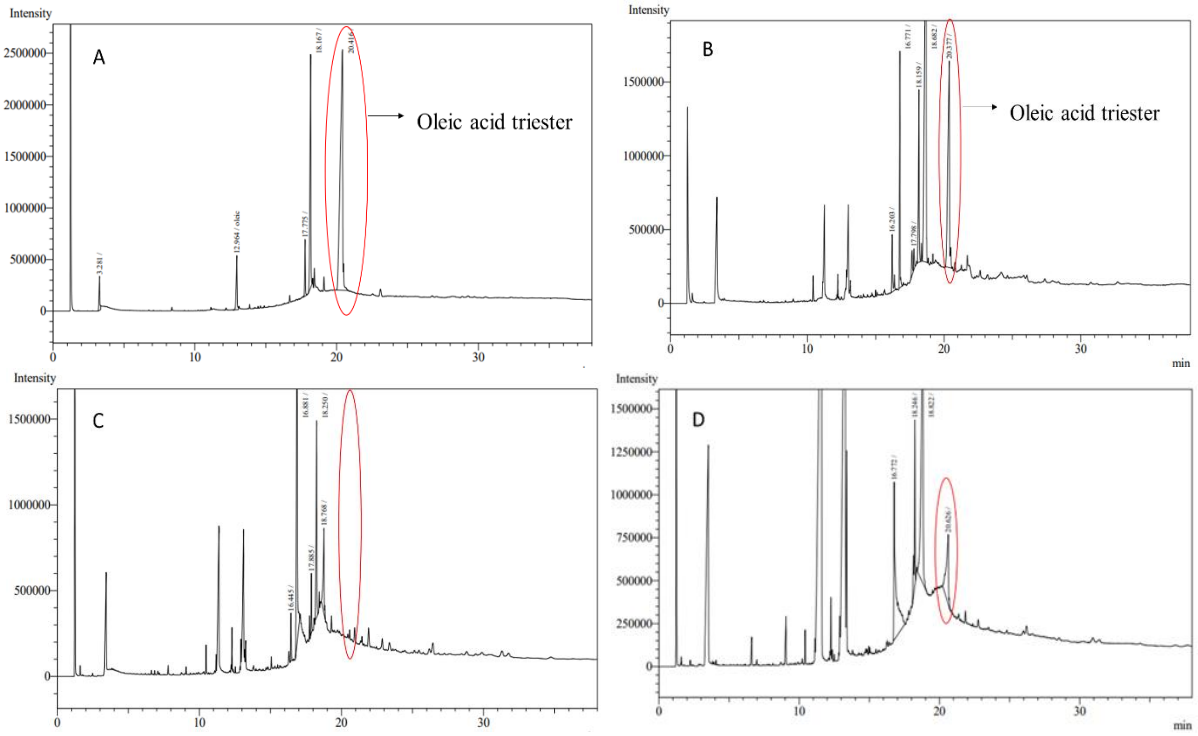

Figure 4. GC-FID chromatogram of the product from esterification of (A) oleic standard with 10% MSA, (B) PFAD with 10% MSA, (C) PFAD with H_2SO_4, and (D) PFAD without catalyst.

Table 6. Lubrication properties of end product compared to other researches.

Property	Method	End product	[18]	[19]	[20]
			TMP triester	Radialube 7121	POME polyol ester
KV @ 40°C (cSt)	ASTM D445-19	68.82	41.76	93	48
KV @ 100°C (cSt)	ASTM D445-19	9.909	8.73	14	8.4
VI	ASTM D2270-14a	126	154	148	152
PP (°C)	ASTM D5950-14	12	-10	-33	5
OIT @ 130°C (min)	ASTM D6186-19	2	254°C*	183°C*	45@ 150°C
Wear scar diameter (mm)	ASTM D4172-18	0.62	n/a	0.81	

KV = kinematic viscosity; VI = viscosity index; PP = pour point; OIT = oxidation induction time; OOT = oxidation onset temperature.
* Reported as oxidation onset temperature (OOT); n/a = Not available

wear on metal surfaces [21]. In this case the end product exhibited satisfactory less WSD compared to the commercial Radialube 7121. The anti-wear property of lubricant depends on many factors e.g., the attraction of polar ester group on metal surface while non-polar fatty acid chain provides slip between surfaces [20].

3.6 Optimization of reaction condition

3.6.1 Mathematical model and ANOVA

The RSM based on the CCD with 2 center points and alpha value of 2 was executed for 26 runs as shown in Table 2. According to the statistical model fit summary, 2Fl model (sequential sum of squares for the two-factor interaction) was suggested as a best fit-model. In the meantime, the ANOVA of two responses (Table 7) indicated that the model was not appropriate for percentage reaction conversion (Y_1). Due to the very low regression, $R^2 = 0.66$ (only about 66% of data fitted to the model). While ANOVA confirmed the adequacy of the model for percentage yield of oleic triester according to P-value < 0.0001 (P-value <0.05 the model term is significance). Furthermore, the $R^2 = 0.97$ and a high value of adjusted- R^2 (0.96) implied that the model was highly significance which conformed with the Predicted- R^2 of 0.92 (only 0.08 cannot be predicted from the model). Therefore, in this study, the 2Fl model would be used only for the percentage yield of oleic triester (Y_2). The final 2Fl model was illustrated as coded factors in Eq. (1).

Percentage oleic triester yield (Y_2) = $32.47 + 0.69X_1 – 0.27X_2 - 0.73X_3 + 3.73X_4 - 0.27X_1X_2 - 0.058\ X_1X_3 - 0.63\ X_1X_4 +0\ .34\ X_3X_3 + 0.18\ X_1X_2 - 0.83\ X_3X_4$ (1)

Table 7. Decisive factor to assess the fitness of the model.

ANOVA	Y_1	Y_2
R^2	0.66	0.97
adjusted R^2	0.44	0.96
Predicted R^2	-0.08	0.92
adeq precision	6.04	27.45
CV %	2.08	2.57
P-value	0.03	< 0.0001

In this study the model accuracy was verified by diagnostic plot of studentized results against the percentage oleic triester yield (Y_2). It could be observed from Figure 5A that the variance of all Y_2 response values were constant due to a randomly distributed point around zero boundary up to ± 3.80725. Additionally, the distribution plot of the actual data and predicted value of Y_2 was highlighted in Figure 5B. In this case, the actual data of Y_2, that came from Table 2, were lied along the predicted values (straight line) obtained from the model. These observations indicated that the model could anticipate the yield of oleic triester (Y_2) that was correspond to actual experiment values. Therefore, the optimization step could be based on this model.

3.6.2 Response surface and optimization

The 3-D surface plot indicated the interaction between input factors to percentage yield of oleic triester as presented in Figure 6 (A-F). The PFAD:TMP molar ratio (X_4) demonstrated the greatest influence while other factor showed much smaller response. The Design Expert 10 software provided the numerical optimization feature that used to determine the optimum solution of all reaction conditions to achieve a maximum yield of oleic triester. Refer to the software solution, the reaction temperature 142.8°C, reaction time 4 h, catalyst loading 1% by weight of PFAD and 3:2 PFAD:TMP molar ration was the optimum reaction condition which 37.83% was an oleic triester yield.

4. Conclusion

This study was proposed to produce triester (polyol ester) as a biolubricant, based on PFAD and TMP by esterification reaction in a presence of MSA as a catalyst. Initially, the screening test was conducted to study the response (reaction conversion) of four factors i.e., reaction temperature, time, catalyst loading and reactant molar ratio, sequentially. The level that presented the highest response of each factor, i.e., 160°C, 6 h, catalyst loading 1.5% by weight of PFAD and 3:1.5 PFAD:TMP molar ratio, was used as a center point for optimization experiment. An optimization was done by using RSM based on CCD and the optimum reaction was 142.8 °C, 4 h, catalyst loading 1% by weight of PFAD and 3:2 with oleic triester yield 37.83%. The lubrication properties of the product, from esterification with center point condition, was analysed. Viscosity index of 126, pour point at 12°C, oxidation induction time at 130 °C for 12 min and wear scar diameter (WSD) of 0.62 mm. These results exhibited a less competitive performance when comparing with triester (from other research) and commercial biolubricant.

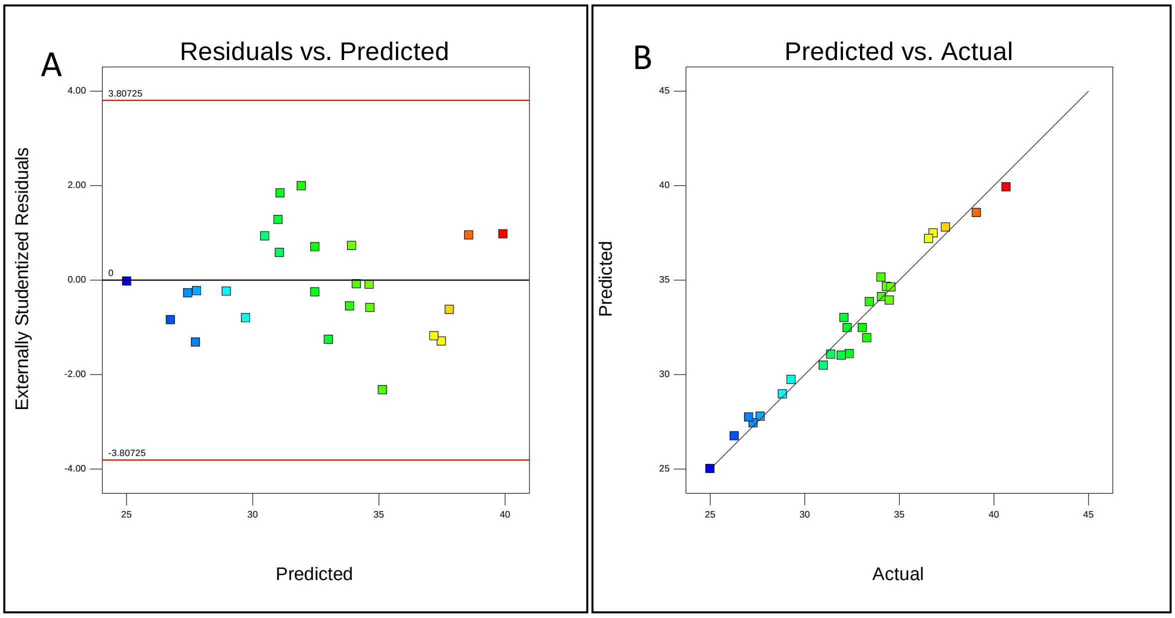

Figure 5. Diagnostic plot of predicted value against actual data of the percentage yield of oleic triester (Y_2).

This might be the low content of triester and the high content of unsaturated species presented in the product. However, the esterification in presence of MSA was proved to promote both the reaction conversion and triester yield.

Acknowledgement

The author would like to express their gratitude to The Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi and the Center of Excellence on Energy Technology and Environment (CEE), Ministry of Higher Education, Science, Research and Innovation for providing funding to do this research work for the financial support provided to perform this study.

References

[1] Salimon, J., Salih, N. and Yousif, E. 2010. Biolubricants: Raw materials, chemical modifications and environmental benefits, *European Journal of Lipid Science and Technology*, 12, 519-530.

[2] Rahim, E. and Sasahara, H. 2011. A study of the effect of palm oil as MQL lubricant on high-speed drilling of titanium alloys, *Tribology International*, 44(3), 309-317.

[3] Shomchoam, B. and Yoosuk, B. 2014. Eco-friendly lubricant by partial hydrogenation of palm oil over Pd/γ-Al_2O_3 catalyst, *Industrial Crops and Products*, 62, 395-399.

[4] Hamdan, S., Chong, W., Ng, J., Chong, C. and Zhang, H. 2018. Nano-tribological characterisation of palm oil- based trimethylolpropane ester for application as boundary lubricant,

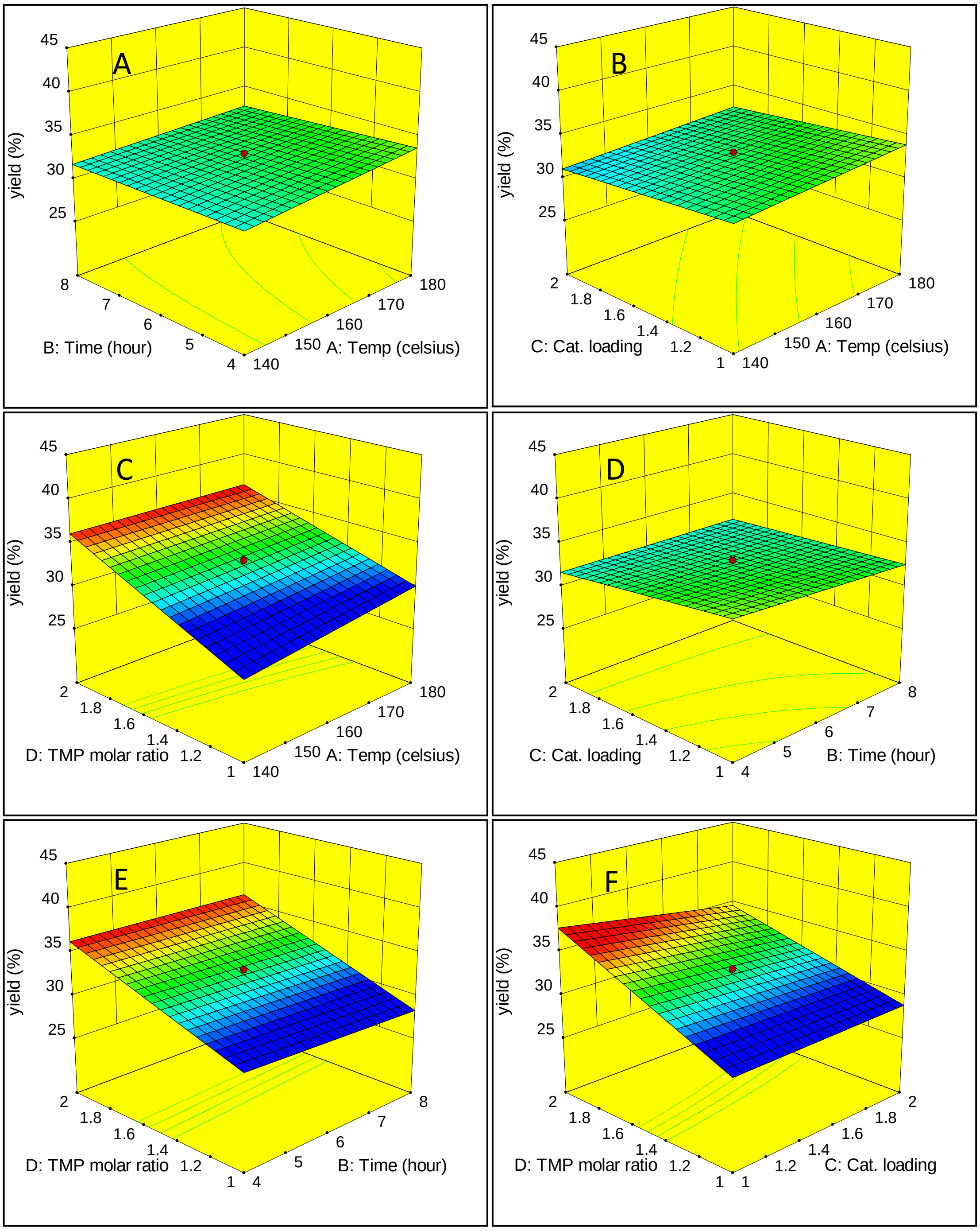

Figure 6. Response surface of percentage oleic triester.

Tribology International, 127, 1-9.

[5] Ho, C.K., Mcauley, K.B. and Peppley, B.A. 2019. Biolubricants through renewable hydrocarbons: A perspective for new opportunities, *Renewable and Sustainable Energy Reviews*, 113, 109261, Available online: https://doi.org/10.1016/j.rser.2019.109261.

[6] Zulhanafi, P. and Syahrullail, S. 2019. The tribological performances of Super Olein as fluid lubricant using four-ball tribotester, *Tribology International*, 130, 85-93.

[7] Nor, N.M., Derawi, D. and Salimon, J. 2018. Synthesis of palm oil fatty acid and trimethylolpropane based ester for biolubricant base stocks, *AIP Conference Proceedings*, 1940, 020095, Available online: https://doi.org/10.1063/1.5028010.

[8] Uosukainen, E., Linko, Y.-Y., Lämsä, M., Tervakangas, T. and Linko, P. 1998. Transesterification of trimethylolpropane and rapeseed oil methyl ester to environmentally acceptable lubricants, *Journal of the American Oil Chemists Society*, 75(11), 1557-1563.

[9] Cavalcanti, E.D., Aguieiras, É.C., Silva, P.R., Duarte, J.G., Cipolatti, E.P., Fernandez-Lafuente, R. and Freire, D.M. 2018. Improved production of biolubricants from soybean oil and different polyols via esterification reaction catalyzed by immobilized lipase from Candida rugosa, *Fuel*, 215, 705-713.

[10] Kefas, H.M., Yunus, R., Rashid, U. and Taufiq-Yap, Y.H. 2019. Enhanced biodiesel synthesis from palm fatty acid distillate and modified sulfonated glucose catalyst via an oscillation flow reactor system, *Journal of Environmental Chemical Engineering*, 7(2), 102993, Available online: https://doi.org/10.1016/j.jece.2019.102993.

[11] Chang, A.S., Sherazi, S.T., Kandhro, A.A., Mahesar, S.A., Chang, F., Shah, S.N., Laghari, Z.H. and Panhwar, T. 2016. Characterization of palm fatty acid distillate of different oil processing Industries of Pakistan, *Journal of Oleo Science*, 65(11), 897-901.

[12] Kulkarni, P. 2015. Methane sulphonic acid is green catalyst in organic synthesis, *Oriental Journal of Chemistry*, 31(1), 447-451.

[13] Ganesan, S., Nadarajah, S., Shamsudin, N.N., Khairuddean, M. and Teh, G.B. 2020. Esterification of palm fatty acid distillate using ammonium ferric sulfate-calcium silicate as a heterogeneous acid catalyst, *BioEnergy Research*, 13(4), 1297-1307.

[14] Ivan-Tan, C.T., Islam, A., Yunus, R. and Taufiq-Yap, Y.H. 2017. Screening of solid base catalysts on palm oil based biolubricant synthesis, *Journal of Cleaner Production*, 148, 441-451.

[15] Silva, M.G., Oliveira, G.S., Carvalho, J.C., Nobre, L.R., Deus, M.S., Jesus, A.A., Oliveira, J.A. and Souza, D.F. 2019. Esterification of oleic acid in a semi-batch bubble reactor for biodiesel, *Brazilian Journal of Chemical Engineering*, 36(1), 299-308.

[16] Antony, J. 2014. Screening designs, *Design of Experiments for Engineers and Scientists* (pp. 51-62) 2nd Ed.

[17] Rakić, T., Kasagić-Vujanović, I., Jovanović, M., Jančić-Stojanović, B. and Ivanović, D. 2014. Comparison of full factorial design, central composite design, and Box-Behnken design in chromatographic method development for the determination of fluconazole and its impurities, *Analytical Letters*, 47(8), 1334-1347.

[18] Bahadi, M., Yusoff, M.F., Salimon, J. and Derawi, D. 2019. Optimization of response surface methodology by D-optimal design for synthesis of food-grade palm kernel based biolubricant, *Industrial Crops and Products*, 139, 111452, Available online: https://doi.org/10.1016/j.indcrop.2019.06.015.

[19] Hoong, S.S., Arniza, M.Z., Mariam, N.M., Armylisas, A.H. and Yeong, S.K. 2019. Synthesis and physicochemical properties of novel lauric acid capped estolide esters and amides made from oleic acid and their evaluations for biolubricant basestock, *Industrial Crops and Products*, 140, 111653, Available online: https://doi.org/10.1016/j.indcrop.2019.111653.

[20] Rakkan, T., Suwanno, S., Paichid, N., Yunu, T., Klomklao, S. and Sangkharak, K. 2017. Optimized synthesis method for transesterification of residual oil from palm oil mill effluent and lipase from Pacific white shrimp (*Litopenaeus vannamei*) hepatopancreas to environmentally friendly biodiesel, *Fuel*, 209, 309-314.