Optimization Process
for the Synthesis of Polyol-Oleates
from Malaysian Unsaturated Palm Fatty Acid Distillate

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ABSTRACT: *Palm Fatty Acid Distillate (PFAD) is a cheap and valuable by-product of edible oil processing industries. Palm fatty acid distillates are generally used in the soap industry, animal feed industry, and as raw materials for oleochemical industries, in the manufacture of candles, cosmetics, and toiletries. Other applications include their use as food emulsifiers, an aid in rubber processing, in the Flavors and fragrance industries well as in pharmaceutical products. Vitamin E has been extracted commercially from PFAD for encapsulation. This study was carried out to determine the optimization conditions for the esterification of Malaysian PFAD with high-degree polyhydric alcohols (TMP, Di-TMP, PE, and Di-PE) in the presence of sulphuric acid as a catalyst based on four reaction parameters; reaction temperature (°C), reaction time (h), the effect of different alcohols, and molar ratios. The results show that a high conversion of 89% USFA-TMP ester was observed at 150°C, the optimal time for the esterification at 6 h to obtain 91% tri-ester yield, TMP ester produced the highest yield percentage (91%) and the optimum molar ratios were 3.5:1 (USFA: TMP), 4.5:1 (USFA-Di-TMP and USFA: PE) and 6.5:1 (USFA: Di-PE).*

KEYWORDS: *Unsaturated palm fatty acid distillate; Esterification; Polyol-oleates; Optimization process.*

INTRODUCTION

Palm Oil Fruit Bunches (FFBs) produce oil from the seed or kernel known as crude Palm Kernel Oil (CPKO) and from the flesh (mesocarp) of its fruit, known as Crude Palm Oil (CPO) [1]. The oil from palm trees must first be processed or refined before humans can safely consume it. Malaysia has one of the most advanced processing industries for palm oil, which started nearly 50 years ago. The processes currently include refining and fractionation either physical or chemical refining. Alkaline refining proves to be a less popular method as compared to physical refining. Some examples of the latter include bleaching earth treatment, phosphoric acid treatment, deacidification (free fatty acids removal), and deodorization (odor removal). Nowadays, high-vacuum conditions together with steam distillation are used to carry out deacidification and deodorization processes to produce refined, bleached, and deodorized palm oil (RBDPO) and a by-product of PFAD. RBDPO is then fractionated into RBDPO olein (RBDPO$_o$) and RBDPO stearin (RBDPO$_s$) for human consumption.

PFAD is a non-consumption by-product from CPO refining process. PFAD is a light brown semi-solid at room temperature melting to a brown liquid on heating [2]. PFAD in general has a bad odor due to minor volatile compounds. PFAD comprises mainly free fatty acids (FFA$_s$) (>80%), minor non-lipids composition, and also glycerol esters. These large amounts of FFA$_s$ and non-lipids compounds in PFAD recovered have their own usages. Oleochemical industries use PFAD as raw material to produce intermediate products. PFAD is traditionally used for the animal feed industry (heaviest users of PFAD) and the soap industry. Vitamin E can also be extracted from PFAD and is known to have many benefits to human health [3]. Nowadays, PFAD is used as the raw material for the production of medium-grade cleaners, bioplastics, and lubricants [4]. Some researchers also point toward the promise of using the free fatty acids (FFA$_s$) extracted from PFAD as raw material for biodiesel production [5-8].

Numerous studies have investigated the physicochemical properties of PFAD [9-12]. Most studies reported that the PFAD properties were definitely affected by the geographic location where the oil palm grows and the refining technology used for CPO refining process. For example, surveys on the characteristics and properties of Palm Fatty Acid Distillate (PFAD) from Malaysian refineries have been conducted by *Ping* and *Yusof* (2009) [13] and others [14, 15]. The results showed that PFAD consists of more than 80% FFA$_s$ comprised of myristic $C_{14:0}$ (1.2%), palmitic $C_{16:0}$ (46.9%), palmitoleic $C_{16:1}$ (0.15%), stearic $C_{18:0}$ (4.3%), oleic $C_{18:1}$ (36.7%), linoleic $C_{18:2}$ (9%), linolenic $C_{18:3}$ (0.3%), eicosanoic $C_{20:0}$ (0.2%) and others (0.1%). These studies seem to be in line with the findings by *Baharudin et al.* (2019) [16] and *Jumaah et al.* (2021) [17] who noted that palmitic acid (47.1%) was the dominant fatty acid in the Malaysian PFAD, followed by oleic acid (36.6%) and linoleic acid (9.6%). Besides that PFAD also consists of 14.4 glycerol, 0.5% vitamin E, 0.8% squalene, 0.4% sterols, and 2.2% others. On the other hand, the composition and characteristics of Thailand's PFAD consisted of 93 wt. % FFA$_s$ and the rest are traces of triacylglycerols, diacylglycerols, monoacylglycerols, and impurities [18, 19]. The FFA$_s$ compose of 45.6% palmitic, 33.3% oleic, 7.7% linoleic, 3.8% stearic, 1.0% myristic, 0.6% tetracosanoic, 0.3% linolenic, 0.3% eicosanoic, 0.2% eicosenoic and 0.2% palmitoleic acid [18]. The composition of the PFAD also depends on the quality of CPO produce which

is related to the level of Palm oil Fruit Bunches (PFBs) ripeness and freshness. Fresh and ripe PFBs produce less free fatty acid in CPO, thus producing less percentage of FFA$_s$ in PFAD composition. On the other hand, less fresh and over-ripe PFBs produce high FFA in CPO. Therefore, it produces a higher percentage of FFA$_s$ in PFAD [16, 20].

Many researchers attempt to isolate and separate saturated palm fatty acids distillate (SFA-PFAD) and unsaturated palm fatty acids distillate (USFA-PFAD) for specific industrial application purposes such as for the production of medium-grade cleaners, biodiesel, bioplastic, and biolubricants. For example, the separation of USFA-PFAD from PFAD through Low-Temperature methanol Solvent Recrystallization (LTSC) has produced significant differences in unsaturated fatty acids composition in its liquid fraction. Under the optimum separation conditions, 93% of USFA-PFAD and 7% of SFA-PFAD in the liquid fraction was reported with 48% yields. Oleic acid as the main unsaturated fatty acid constituent surged from 37.6% in PFAD to 76% in USFA-PFAD, while the main saturated palmitic acid constituent declined from 49% in PFAD to 6.2% in USFA-PFAD [17, 21, 22]. Both USFA-PFAD and SFA-PFAD can be used for their own specific industrial application.

The chemical industry is highly dependent on the esterification process where it uses ester products for making cosmetics, paints or solvents, emulsifiers, biodiesel, and biolubricants [23]. The process should be industrial feasible and cost-effective. One way of cost-effective approach is by minimizing the number of unnecessary experiments number [24]. Therefore, evaluating and solving problems in the esterification studies can be done by adopting the optimization process approach. The objective of optimization is to develop an effective correlation among the esterification reaction process independent factors that effectively control the reaction conditions [25]. To develop an ultimate effective correlation of the esterification process, it is essential to garnering significant information about the reaction, such as the interaction between independent factors. Hence, different experiments are carried out in line with the optimization to generate an effective correlation that provides the best performance of the esterification process for future purposes. The information in the target esterification reaction process can be derived experimentally, and the hypothesis can be substantiated or negated by the

experimental results. The optimization process optimizes the process parameters by carrying out requisite experiments and elucidating the significant behavior of the process based on the experimental results. The evaluation of the esterification process requires two variables: factor and response. The factor controls the responses which provide information on the performance of the esterification process. Factors can be set on a range of values (more than two) and can be divided into groups. A response is the outcome of changes in the factors of a process, where multiple responses are identified [26]. Optimization is required after the significant factors of the process have been identified by the screening experiments. In the optimization process, the effects of factors and their interaction lead to the production of the best response with detailed information from the experiments. This simply means that the optimization process helps to create effective optimal conditions for the esterification process [27].

This work aims to discuss the optimization process for the synthesize of polyol-ester from the esterification reaction of unsaturated palm fatty acid distillate (USFA-PFAD) with different kinds of polyhydric alcohols [trimethylolpropane (TMP), di-trimethylopropane (di-TMP), pentaerythritol (PE) and dipentaerythritol (di-PE)] and study the effect of several variable independents factors that affect the esterification yield and polyol-ester selectivity.

EXPERIMENTAL SECTION
Materials
In this study, PFAD was obtained from a local refinery, Sime Darby Plantation Berhad (647766-V), located in Selangor, Malaysia. USFA-PFAD represented by oleic acid (76%) was separated from PFAD by low-temperature methanol crystallization [22] and used as received. All chemicals used in this work as methanol, polyhydric alcohols, ethyl acetate, toluene, sulfuric acid, sodium bicarbonate, sodium sulfate, and saturated sodium chloride were all analytical grade and used without further purification. Polyhydric alcohols used were pentaerythritol (PE), di-pentaerythritol (di-PE), trimethylolpropane (TMP), and di-trimethylolpropane (di-TMP) purchased from Sigma Aldrich Chemical Co (Malaysia).

Esterification reaction
Four PFAD esters were synthesized from an esterification reaction between unsaturated fatty acid with various high-degree polyhydric alcohols according to *Arbain* and *Salimon* [28]. In a flask with a reflux condenser and three necks, fatty acids were mixed with polyhydric alcohols 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 (25 mL), and the product was transferred into 100 mL separation funnel, then added 10 mL saturated sodium bicarbonate ($NaHCO_3$) and shaken. The funnel was left until two layers formed. The aqueous layer at the bottom was removed, leaving the organic layer. $NaHCO_3$ 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 formation 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 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.

Characterization of polyol-ester
The composition of the polyol-ester fatty acids was determined using the gas chromatography method according to ASTM D6186 method. The sample was initially prepared by adding exactly 0.5 mL of homogenized sample into a vial of 10 mL; then 100 mL of *N*-methyl-*N*-trimethylsilytrifluoroacetamide (MSTFA) were added. After 20 min, GC-grade ethyl acetate (5 mL) was added and swirled. After thorough swirling, the sample was then heated in the 40 °C water bath for about 10 min. The sample was left to cool to room temperature

then injected on the Shimadzu, 17A GC-FID equipped with column BPX 70 (30 m x 0.25 mm x 0.01 μm film thickness; SGE) [29]. The analysis of ester composition in polyol-esters was performed by using a DB-5HT (30 m x 0.25 mm x 0.01 μm). Helium, as the carrier gas for the GC system, was injected at a flow rate of 1 mL of the sample. The injector and detector were adjusted at 380 and 400 °C, respectively. The oven temperature was set to 100 °C for 1 min during the first holding time. The ramping rate was elevated to 5 °C/min until 380 °C has been reached, and it was kept constant for 80 min. Parameters of the GC were adopted according to *Arbain* and *Salimon* [28]. The peaks were identified by comparing the retention time to authentic standards. All measurements were at least triplicate and reported with ± standard deviation.

RESULTS AND DISCUSSION
Esterification reaction of USFA PFAD

A series of esterification reactions were performed between USFA PFAD:TMP (3:1), USFA PFAD:Di-TMP (4:1), USFA PFAD:PE (4:1), and USFA PFAD:Di-PE (6:1) in the presence of 2% (wt.) of concentrated sulphuric acid (H_2SO_4) as a catalyst. Four unsaturated USFA-polyol-esters known as USFA-TMP ester; USFA-Di-TMP ester; USFA-PE ester and USFA-Di-PE ester were synthesized as shown in Figs. 1-4.

USFA-Trimethylolpropane Ester

Fig. 1 shows the esterification reaction between 3 moles of USFA PFAD with 1 mole of trimethylolpropane (TMP). H_2SO_4 (2%) was used as a catalyst at 150 °C for 6 h. The oleic acid was chosen as the representative of USFA fatty acids due to its domain composition in the ratio of oleic acid: linoleic acid (4.4: 1). The reaction product was USFA-TMP tri-oleate and water molecules as by-products. The water was continuously removed during the esterification reaction steps. The yield percentage of USFA-TMP tri-oleate was 91% and tri ester composition was 87%.

USFA- Di-Trimethylolpropane Ester

Fig. 2 shows the esterification reaction between 4 moles of USFA PFAD with 1 mole of di-trimethylolpropane (Di-TMP). H_2SO_4 (2% wt.) was used as a catalyst and the reaction occurred at 150 °C for 6 h. The reaction had produced USFA-Di-TMP tetra-oleate
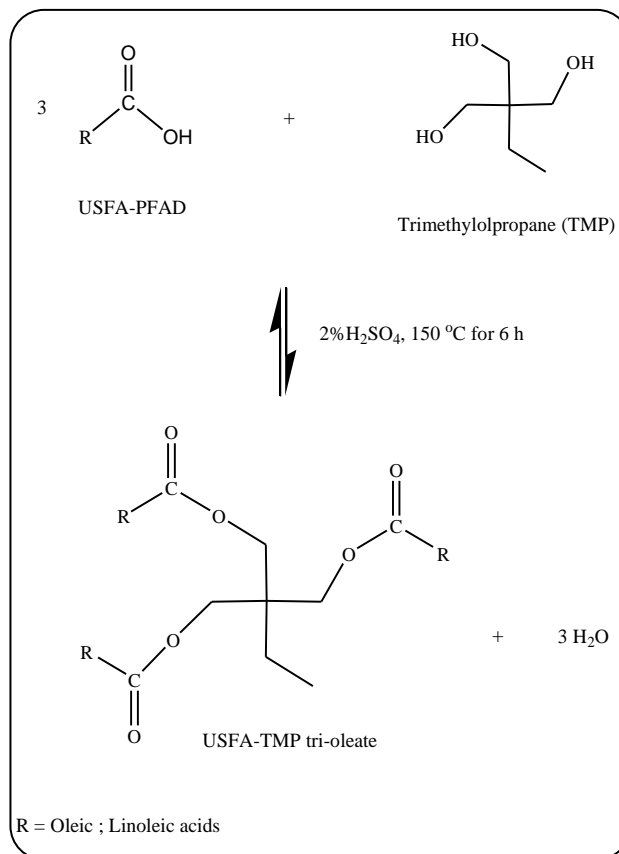

Fig. 1: Esterification reaction to form USFA-TMP tri-oleate.

and water molecules (by-product). The yield percentage of USFA-Di-TMP tetra-oleate was recorded as 88% and the tetra-ester composition was 88%.

USFA- Pentaerythritol Ester

Fig. 3 shows the esterification reaction between 4 moles of USFA PFAD with 1 mole of pentaerythritol (PE). The catalyst H_2SO_4 (2%) was used as a catalyst at 180 °C for 6 h reaction time. The reaction product was USFA-PE tetra-oleate and water molecules (by-products). The yield percentage of USFA-PE tetra-oleate was 86% and tetra-esters composition was 83%.

USFA- Di-Pentaerythritol Ester

Fig. 4 shows the esterification reaction between 6 moles of USFA PFAD with 1 mole of di-pentaerythritol (Di-PE). H_2SO_4 (2%) was used as a catalyst at 180 °C reaction temperature for 6 h. The reaction product was USFA-Di-PE hexa-oleate and water molecules (by-products). The yield percentage of USFA-Di-PE hexa-oleate was 83% and hexa-esters composition was 80%.
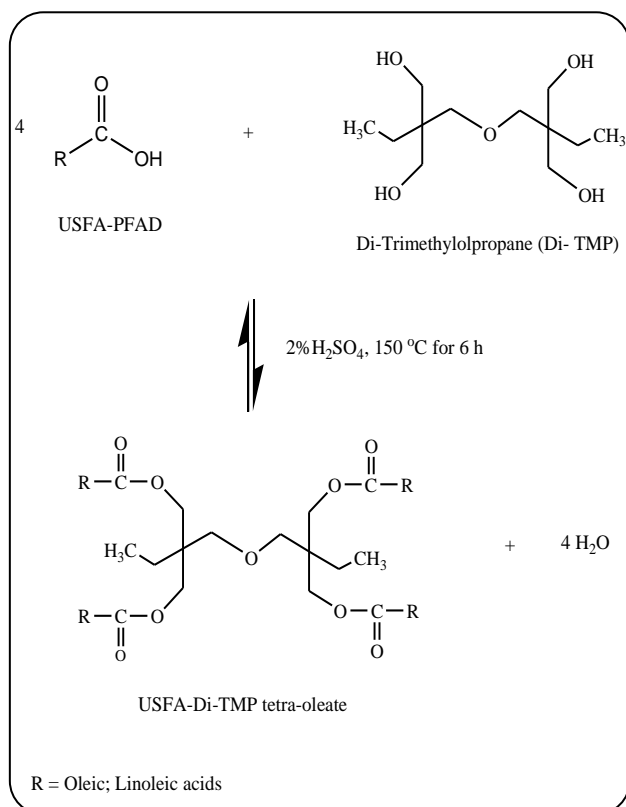
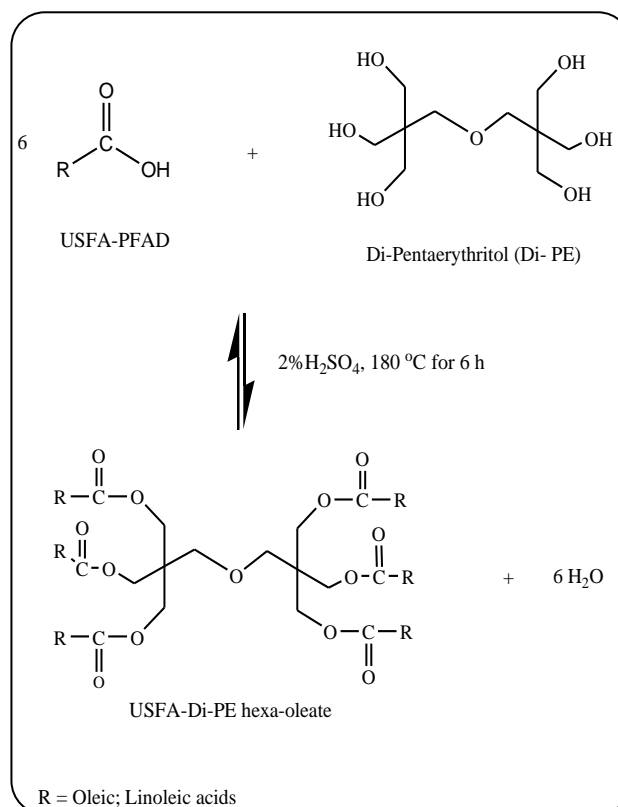**Fig. 2: Esterification reaction to form USFA-Di-TMP tetra-oleate.**

Fig. 4: Esterification reaction to form USFA-Di-PE hexa-oleate.
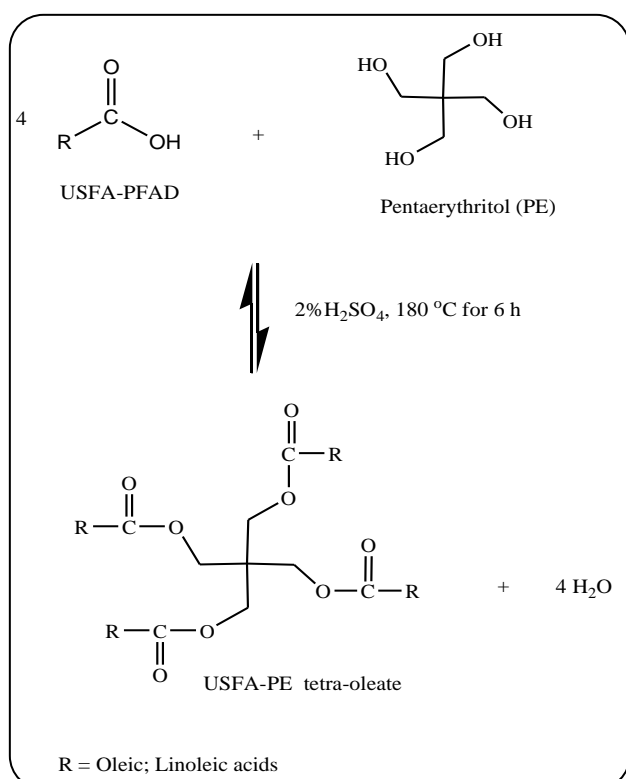

Fig. 3: Esterification reaction to form USFA-PE tetra-oleate.

Optimization of esterification reaction conditions

High esterification responses of yield and polyol-ester composition percentage were attempted through the optimization process for all esterification reactions of USFA PFAD with TMP, Di-TMP, PE, and Di-PE. The optimization was investigated by varying the independent reaction variables such as temperature, time of the reaction, type of polyhydric, and the amount of catalyst used. Therefore, by optimization process, the effective correlation among the esterification reaction process independent factors can be understood and developed for an effective control of the esterification reaction conditions. Thus, higher yield and polyol-ester composition percentage can be gathered at the optimal reaction condition.

In this study, the esterification temperatures for the optimization process were investigated in the range of 110 -150 °C for low melting point polyhydric alcohols such as TMP and Di-TMP. Meanwhile, high melting points for PE and Di-PE were selected from 150 - 200 °C, respectively. The other reaction factors were kept constant with 2% (w/w) of H_2SO_4 catalyst and 5 h of reaction time was used for
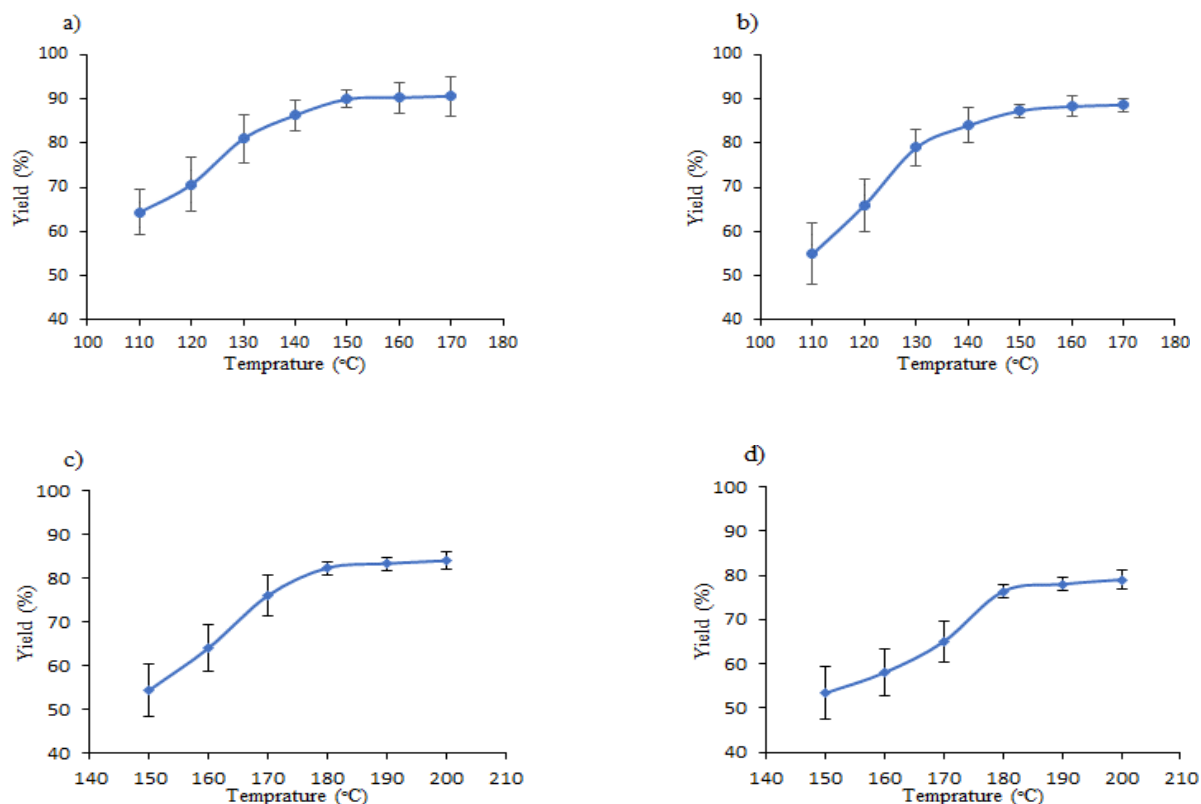
Fig. 5: Effect of esterification temperature on yield of polyol-esters at 5h and 2% H_2SO_4 for (a) USFA-TMP (3:1), (b) USFA-Di-TMP ester (4:1), (c) USFA-PE (4:1) and (d) USFA-Di-PE ester (6:1).

the esterification reaction condition. Fig. 5 shows the production of USFA-TMP ester, USFA-Di-TMP ester, USFA-PE ester, and USFA-Di-PE ester at different temperatures. A high conversion yield of 89% for USFA-TMP ester and 87% for USFA-Di-TMP ester was obtained at 150 °C. Meanwhile, as high as 82% of USFA-PE ester and 78% of USFA-Di-PE ester were achieved at optimized temperature conditions at 180 °C. During the esterification reaction, the intermediate products of polyol mono-, di-, tri-, tetra-, and hexa-esters will be produced before the final ester product conversion. The final esters product for the esterification reactions will be USFA-TMP tri-ester, USFA-Di-TMP tetra-ester, USFA-PE tetra-ester, and USFA-PE hexa-ester, respectively. An increase in reaction temperature will increase the yield of ester formation for all reactions of USFA PFAD with TMP, Di-TMP, PE, and Di-PE. However, a slight decrease in yield ester formation was observed after the optimum temperature was reached. This shows that the temperature factor contributes significant corelation toward the esterification reaction yield [30].

The duration of the esterification reaction time is another important factor to obtain a high yield of desirable esters. The optimization process was next investigated for the effect of the esterification time reaction. The esterification reactions were carried out at reaction time in the range of 4 - 8 h and other reaction factors were kept constant with 2% (wt.) of H_2SO_4 catalyst and at the reaction temperature of 150 °C for USFA PFAD-TMP and USFA PFAD-Di-TMP, whereas of 180 °C for USFA PFAD-PE and USFA PFAD-Di-PE, respectively. Fig. 6 shows the esterification reaction results when the time was varied up to 8 h. This was taking into account the fact that polyhydric alcohol used took 1 to 2 h to completely melt before undergoing an effective reaction. Thus 4 h time was used to report the result in view that the effective starting point for the reaction. It can be observed that the higher the reaction time the higher the reaction yields for all polyol-esters. The results showed that the optimal reaction time for the esterification reaction time to produce 91% yield of USFA-TMP tri-ester was at 6 h. The same optimal
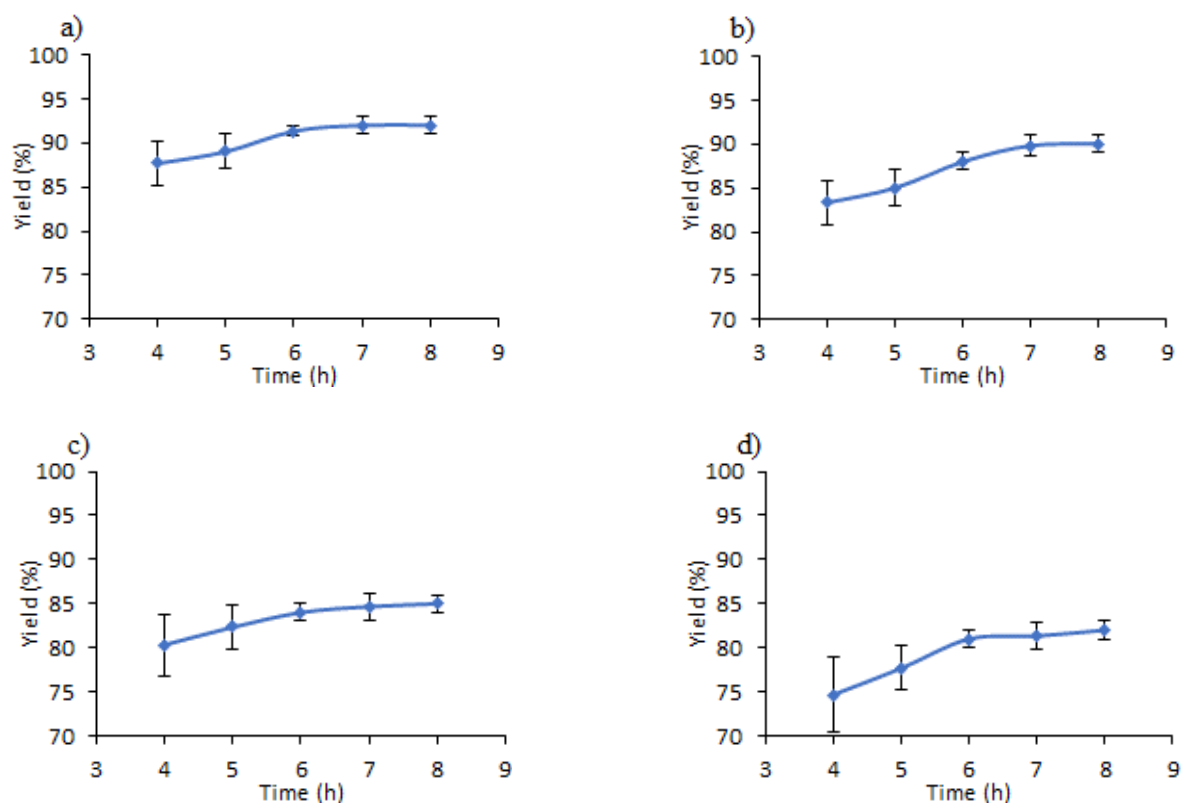
Fig. 6: Effect of esterification time on USFA esters yield using 2% H_2SO_4 for (a) USFA-TMP (3:1) at 150 ^{o}C, (b) USFA-Di-TMP ester (4:1) at 150 ^{o}C, (c) USFA-PE (4:1) at 180 ^{o}C and (d) USFA-Di-PE ester (6:1) at 180 ^{o}C.

reaction time at 6 h was recorded for other polyol-esters with 88% yield of USFA-Di-TMP, 84% yield of USFA-PE tetra-ester, and 80% yield of USFA-Di-PE hexa-ester, respectively.

The ester yield percentages vary according to the chemical structure of polyhydric alcohol used. Fig. 7 shows the effect of different polyhydric alcohols on the polyolester yield percentage. Among several branched polyhydric alcohols used in the current study, TMP with less-branched hydrocarbon chains produces the highest yield percentage of USFA-TMP tri-ester (91%). On the other hand, the more-branched polyhydric alcohol of Di-PE produces the lowest yield percentage of USFA-Di-PE hexa-ester (81%). This result may due to the fact that the less-branched hydrocarbon chain in the alcohols (TMP) exhibits less steric hindrance and thus enhanced the rate of esterification as compared to more-branched polyhydric alcohol (Di-PE). The higher rate of reactions produced higher yield percentages [31]. The steric hindrance in more-branched Di-PE which slowing down the chemical
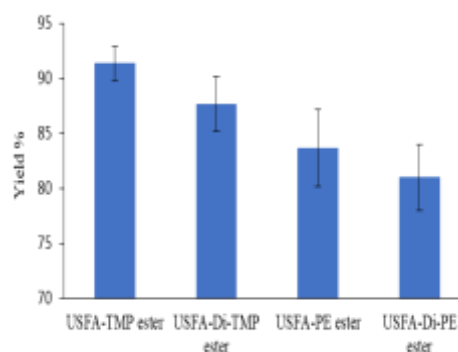

Fig. 7: Effect of different polyhydric alcohols on USFA esters yield.

reaction due to the blocking, repulsion, and less attached site for the reaction to occur.

An adequate and availability of the reactants in terms of the molar ratio of polyhydric alcohol to USFA PFAD are important parameters to be studied. At least three different molar ratios of USFA PFAD to each polyhydric alcohol
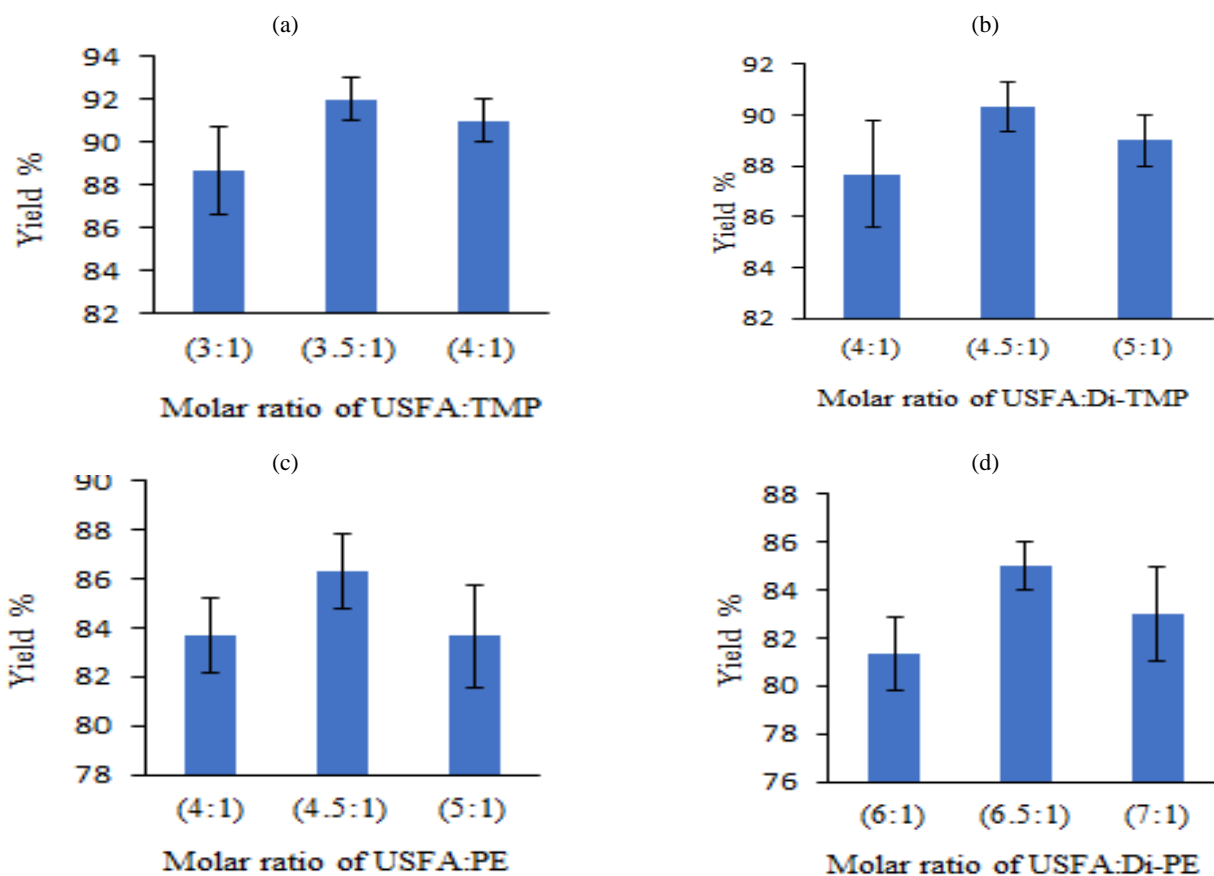
Fig. 8: Effect of molar ratio of USFA and different polyhydric alcohols on the USFA esters yield (%) with 2% H₂SO₄ at 6 h and 150 °C for (a) USFA-TMP and (b) USFA-Di-TMP and at 180°C for (c) USFA-PE and (d) USFA-Di-PE.

were selected as shown in Fig. 8 to investigate the effect of the reactant's molar ratio on the reaction yield. The results showed that an excess of polyhydric alcohol in the reaction system increased the polyol-ester yield by shifting the equilibrium of the reaction more to the right. Thus increasing the esterification products. The optimal reactants molar ratios were obtained at 3.5:1 to produce USFA-TMP tri-ester, 4.5:1 for USFA-Di-TMP tetra-ester, 4.5:1 for USFA-PE tetra-ester and 6.5:1 for USFA-Di-PE hexa-ester.

Ester composition

The esterification processes occurred in this study produced four types of polyol-esters known as USFA-TMP tri-oleate, USFA-Di-TMP tetra-oleate, USFA-PE tetra-oleate, and USFA-Di-PE hexa-oleate. The ester composition in each polyol-ester needs to be evaluated for confirmation of complete esterification processes have been achieved. For example, the USFA-TMP tri-ester composes three ester functional groups. This can

be confirmed by using high-temperature column GCFID analysis. Fig. 9 shows the high-temperature column GCFID chromatogram for USFA-TMP tri-oleate. The result showed that nearly 99% ester composition was the major tri-ester which the tri-ester peaks started to form at a retention time (R_T) of 51.20 minutes. Whereas the composition of mono- and di-ester appeared in trace amounts. This indicates the success of the esterification process through the conversion of TMP polyhydric OH group to ester functional group [32]. Further confirmation on fatty acid composition in USFA-TMP tri-ester, the product was analyzed for its methyl ester composition by GC-FID equipped with a non-polar DB-5 column. Fig. 10 shows USFA-TMP tri-ester composes of palmitic acid (6%), oleic acid (76%), and linoleic acid (18%) that nearly the same fatty acid composition of USFA PFAD raw material. This result also approved that correct fatty acid representation in USFA PFAD was used as a theoretical esterification chemical reaction in this study.
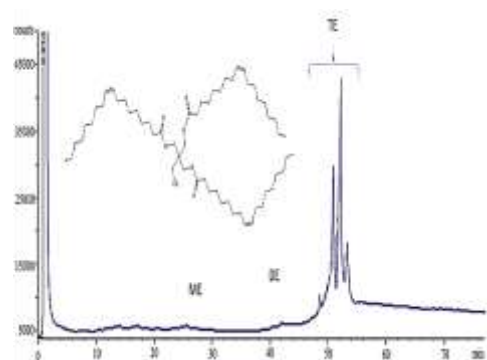
Fig. 9: GC chromatogram for ester composition of USFA-TMP tri-ester. Note: ME = Mono-ester, DE = Di-ester and TE = Tri-ester.
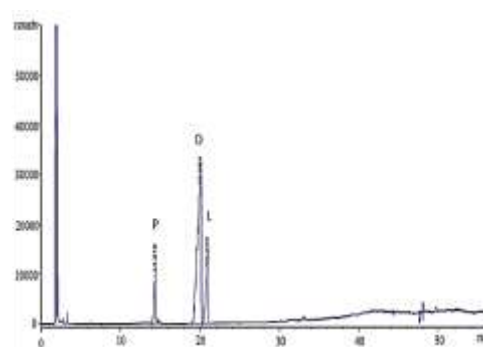

Fig. 10: GC chromatogram for fatty acid composition of USFA-TMP tri-ester. Note: P = Palmitic acid, O = Oleic acid and L = Linoleic acid.

CONCLUSIONS

The esterification reaction of USFA PFAD with four different types of polyhydric alcohols (TMP, Di-TMP, PE, and Di-PE) was successfully carried out to produce the corresponding esters; USFA-TMP tri-ester, USFA- Di-TMP tetra-ester, USFA-PE tetra-ester, and USFA-Di-PE hexa-ester. The optimization proses were effectively adopted to investigate the correlation and the effect between the esterification independent variable parameters. All polyol-esters were produced at high conversion yield with high polyol-ester composition at their esterification optimal condition. Polyhydric alcohol with less branched carbon chain (TMP) has resulted in the highest reaction yield and ester composition of resultant polyolester.

Acknowledgments

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