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# Production of High Oleic Palm Oils on a Pilot Scale

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Abstract Refined, bleached and deodorized palm olein (RBD POo) with an iodine value (IV) of 62 was chemically interesterified with methyl oleate (MO) at a ratio of 50:50 (w/w). The reaction was carried out at 110  $^{\circ}$ C in the presence of sodium methoxide as a catalyst using a 100-kg pilot scale reactor. Randomization between 15 and 30 min resulted in less free fatty acid (FFA) formation and higher oleic content in the interesterified product as compared to longer reaction time of 60–90 min. Sodium methoxidecatalyzed ester interchange increased the oleic content of the interesterified product to more than 57% from its initial content of 45%. The product obtained also has an IV of more than 75. The interesterified oil was then subjected to dry fractionation in a 200-kg De Smet jacketed crystallizer at  $8^{\circ}$ C to further enhance the oleic content of the liquid olein fraction. The resulted olein had an improved cloud point and higher IV of 81. The solid stearin had a slightly higher IV and oleic content as compared to normal palm stearin. The solid fat content was comparable to normal palm oil. The pilot scale study has proven a successful conversion of laboratory findings to a larger scale

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production and gave the most realistic information for possible commercialization.

**Keywords** Interesterification  $\cdot$  RBD palm olein  $\cdot$ Methyl oleate · Sodium methoxide · Fractionation

# Introduction

Palm oil consists of mainly saturated and monounsaturated fatty acids. Palmitic acid (44.0%) is the most abundant fatty acid found in palm oil followed by oleic acid at 39.2% [\[1](#page-7-0)]. These fatty acids are attached to the glycerol backbone, forming a variety of triacylglycerols. Fractionation of palm oil separates the low and high melting triacylglycerols into two fractions, namely olein and stearin respectively. Palm olein contains 37.9–41.7% of palmitic and 40.7–43.9% of oleic acid. Palm stearin on the other hand has 47.2–73.8% and 15.6–37.0% of palmitic and oleic acid, respectively [\[2](#page-7-0)]. Most of the monounsaturated fatty acids found in palm olein were located in the sn-2 position in the glycerol backbone whereas the sn-1,3 positions are largely occupied by saturated fatty acids [[3\]](#page-7-0).

The main disadvantage of establishing palm products, especially palm olein, in temperate countries as retail products is their cold stabilities. Siew et al. [[4\]](#page-7-0) noted that palm olein of IV 60 crystallizes at  $5^{\circ}$ C in 3 h and within 1 day at temperatures up to 20  $^{\circ}$ C. Palm olein with IV of 65 may be stable at 20  $^{\circ}$ C for at least 1 month, but also crystallizes at 10  $\mathrm{^{\circ}C}$  within 1 day. Nor Aini et al. [\[5](#page-7-0)] found that IV 65 palm olein remained clear up to 2 months at 20  $\degree$ C and only 1 day at 5  $\degree$ C. Blending with other soft oils may improve the cold stability of the oil blend.

Interesterification of oils and fats, either chemically or enzymatically significantly alter the physical and

functional properties of the starting materials as a result of random or direct rearrangement of fatty acid in triacylglycerol. Earlier workers had discussed the effect of interesterification on melting/dropping point, crystallization, solid fat content  $[6–11]$  $[6–11]$  as well as the oxidative stability of interesterified oils/blends [\[12–14](#page-7-0)]. Interesterification of high melting fat with liquid oil will further reduce the melting point and solid fat content at various temperatures of the fat [\[10](#page-7-0)]. Laning [[6](#page-7-0)] reported that chemical interesterification not only alters the melting characteristic of palm, palm kernel and coconut oils but may also influence crystal morphology and rate of crystal formation. Marangoni and Rousseau [[7\]](#page-7-0) studied the influence of chemical interesterification on melting and crystallization properties of blended palm oil with soybean oil and lard with canola.

To improve the properties and quality, the interesterified products are further fractionated to obtain two fractions as the melting point of the starting material is increased after successful randomization. Fractional crystallization or the fractionation process is based on differences in melting of the component triacylglycerols and partial glycerols [\[15](#page-7-0)– [17\]](#page-7-0). It is a thermal mechanical separation process where the low and high melting triacylglycerols are separated by partial crystallization, followed by filtration [\[18](#page-7-0)]. The liquid and solid fractions which were dominated by the respective low- and high-melting TAGs showed a significant difference in physical and chemical properties from the original oil  $[19]$  $[19]$ . Timms  $[20]$  $[20]$  reported that the quality of the liquid fraction depends only on the crystallization step, whereas the quality of the solid fraction depends on both the crystallization and separation steps. The fractionated olein will have an improved cold stability as well as cloud point due to separation of the high-melting TAGs.

Pilot plant studies are usually carried out after successful laboratory experiments. It is an important tool for monitoring the feasibility and reliability of a newly developed process. The results obtained from the pilot plant trials are also applicable to the industrial conditions. In a hydrogenation process to produce shortening stocks, pilot plant reactor gave a better recovery of palladium catalyst as compared to laboratory experiments [[21\]](#page-7-0). In addition, large scale research could be beneficial for improving the quality and productivity in the production of structured lipids [\[22](#page-7-0)].

Oil producers around the world started to produce high oleic oils several years back. The increased world demand for high oleic oils resulted in the expansion of high oleic sunflower cultivation in Europe. It is predicted that the market share for palm olein will drop in the next few years especially for the application of palm olein in frying. In order to ensure that palm oil does not lose its market share, the Malaysian Palm Oil Board (MPOB) has embarked on a programme of research to produce high oleic oils. The research includes breeding, genetic modification and chemical methods.

The aim of this study was to produce high oleic palm oils on a pilot scale. Laboratory experiments had been successful in producing such oils.

## Materials and Methods

## Materials

Refined, bleached and deodorized palm olein (RBD POo) with an IV of 62 was purchased from a local refinery (Golden Jomalina Food Industries Sdn. Bhd., Klang, Selangor, Malaysia), methyl oleate (MO), which is a distillate of palm-based methyl ester was purchased from the Lion Corporation, Japan, sodium methoxide in powder form was purchased from Fluka Chemie GmbH (Germany) and citric acid in granular form was purchased from SYSTERM Chemical Sdn. Bhd., bleaching clay, Taiko Supreme 1B was purchased from Taiko Clay Marketing Sdn. Bhd., Perak, Malaysia. All reagents used were of analytical grade.

## Interesterification Procedure

Sodium methoxide-catalyzed ester interchange was carried out in a 100-kg stainless steel loop reactor equipped with mixing chamber on the top. 50 kg of RBD POo and 50 kg of MO were mixed in the reactor and dried at 135  $\degree$ C for 30 min under a vacuum of 50 mbar. The mixture was then cooled to 110 °C under atmospheric pressure before the introduction of 200-250 g  $(0.2-0.25\% \text{ w/w})$  of sodium methoxide. Later, 2.2 L of citric acid at 25% concentration (w/v) was added into the mixture to terminate the reaction. The interesterified mixture was transferred to a second reactor equipped with an agitator for further treatments.

In the second reactor, hot water at 90  $^{\circ}$ C was used to wash out any soap produced from the side reaction. A quantity of 20 L of hot water was used for each washing. The washing process was carried out in triplicate before the interesterified mixture was dried. After that, 500 g (0.5% w/w) of bleaching earth was added for post refining of the mixture.

## Short Path Distillation

Short path distillation was used to separate the MO as well as other by-products. The interesterified mixture was first pre-treated in a falling film evaporator before separation in the short path distillation. The falling film evaporator and short path distillation were operated at 160 and 200 °C with a vacuum pressure of 29 and 0.001 mbar,

respectively. The initial flow rate for the distillation was at 10–12 kg/h before a higher flow rate of 25–30 kg/h was applied to the system. High oleic palm oil (HOPO) was collected as the residue and recycle MO was recovered as the distillate. Several batches of HOPO were prepared for further fractionation of the product.

#### Dry Fractionation

Approximately 120–140 kg of HOPO was fed into a 200-kg double-jacketed De Smet crystallizer. It was heated at 70  $\degree$ C with agitation for 2 h to eliminate any nuclei present in the oil. The oil was then cooled gradually according to a predetermined cooling program. The agitation was between 10 and 30 rpm. The cooling program and agitation rate were controlled by a Wizcon Programmable Controller (De Smet, Brussels, Belgium). Fractionation was carried out at 8 °C as higher temperatures produced considerably little amount of the stearin while lower temperatures require too long a cooling cycle.

The slurry was then subjected to physical separation by means of dry fractionation. A filter press designed by Welders Filtration Technology (Aalst, Belgium) was used for filtration. The filter press consists of membrane plates and filter chambers. Prior to filtration, the filter press was chilled to an almost similar temperature to that of the slurry's temperature to avoid deformation of crystals and minimum crystal damage during filtration. Filtration was carried out with the assistance of a volumetric pump. The slurry was first fed into the filter press with a minimum pressure rate of 0.5 bar/min. The filling period was 10 min with a maximum pressure of 2.5 bars. After the maximum pressure was achieved, squeezing of the stearin cake inside the chamber was resumed. Squeezing was carried out by pumping chilled water into the filter membrane plates. During squeezing, pressure was applied to the pressuring side of the membranes, compressing the stearin cake and expelling more liquid fraction. The stearin cake was squeezed at a rate of 0.5 bar/min for the first 10 min and at a rate of 1 bar/min for the last 10 min. The maximum pressure applied was 20 bar [[23](#page-7-0)]. After squeezing of the cake was complete, the filter press was opened and the stearin cake was collected in a hopper located underneath the filter. Olein and stearin fractions were weighed and analyzed.

#### Fatty Acid Composition (FAC)

Fatty acid methyl esters (FAMEs) were prepared by a rapid method [[24\]](#page-7-0). The oil was transesterified with 0.5 M sodium methoxide. n-Hexane (0.95 mL) was added to the oil sample in a 2-mL glass vial using a graduated pipette. The mixture was shaken vigorously with a vortex mixer to dissolve the oil. Sodium methoxide (0.05 mL) was then added using a pipette. The vial was well shaken with a vortex mixer for 5 s. After 5 min, the clear upper layer of methyl esters was pipetted off for GC analysis.

Quantification of the peak areas was carried out with a Hewlett-Packard HP5890 II gas chromatograph equipped with a flame ionization detector and a fused-silica capillary column (60 m  $\times$  0.25 mm i.d., 0.25 µm film; J&W Scientific, Folsom, CA, USA). The analysis conditions were based on the Malaysian Palm Oil Board (MPOB) Test Method p3.5: 2005 and also corresponded to those described by others [[25,](#page-7-0) [26\]](#page-7-0). A correction based on the RM-6 FAME Standard (Supelco Inc., Bellefonte, PA, USA) was used for calculation of the weight percentage of the total mass.

#### Iodine Value (IV)

The Iodine Value (IV) was calculated from the composition of the unsaturated methyl esters.

## Triacylglycerol (TAG) Composition

Determination of individual triacylglycerols (TAGs) by high performance liquid chromatography (HPLC) was done according to IUPAC (1992) Standard Method 2.325 [\[27](#page-7-0)]. The HPLC set-up used consisted of Gilson 303 and 302 pumps, a Waters 410 differential refractometer and a Hewlett Packard 3396A integrator. The two columns used were  $25 \text{ cm}$  long, 4 mm i.d., and packed with  $5 \text{ }\mu\text{m}$ Lichrosphere RP18 (Merck, Darmstadt, Germany). The columns were kept in an oven at 30  $^{\circ}$ C. The mobile phase was acetone:acetonitrile (75:25, v/v) at a flow rate of 1.0 mL/min. Injection was achieved through a Rheodyne valve fitted with a 20-µL loop. Samples were injected as 10% (w/v) solutions in warm acetone. Identification of the TAGs was made by comparison with those of available standards, purchased through Sigma Chemical Co., St-Louis, MO, USA.

# Cloud Point (CP) Test

The oil sample (45 g) was filtered, heated to 130  $\degree$ C for 5 min and poured into a sample bottle. The bottle and sample were cooled in a water bath and continuously stirred for uniform temperature. When the sample reached a temperature of about 10  $\mathrm{^{\circ}C}$  above the CP, rapid stirring in a circular motion was applied to prevent supercooling and solidification of fat crystals on the side or bottom of the bottle. The test bottle was maintained in such a position that the upper level of the sample in the bottle was level with the water in the bath. The bottle was removed from the bath and the sample was inspected for clouding regularly. The temperature at which that portion of thermometer immersed in the oil was no longer visible when viewed horizontally through the bottle and sample was reported as the CP, as described in AOCS (1998) Official Method Cc 6-25 [[28\]](#page-7-0).

## Slip Melting Point (SMP)

Slip melting point (SMP) was determined by the AOCS (1998) Official Method Cc 3-25 [[28\]](#page-7-0). Six capillary tubes were each filled with a 10-mm-high column of fat. The fat column was chilled by holding and rolling the ends of the tubes containing the sample pressed against a piece of ice until the fat solidified. The tubes were placed in a test tube and held in a beaker of water equilibrated at  $10 \pm 1$  °C in a thermostated water bath. The beaker was transferred to the water bath and held for 16 h at  $10 \pm 1$  °C. The capillary tubes were then removed from the test tube and attached to a thermometer with a rubber band so that the lower ends of the tubes were level with the bottom of the mercury bulb of the thermometer. After that, the thermometer was suspended in a beaker containing 400 mL boiled distilled water such that the lower end of the thermometer was immersed in the water to a depth of 30 mm. The starting temperature of the bath was adjusted to  $8-10$  °C below the expected SMP of the sample. The water was agitated with a magnetic stirrer and heat was applied to increase the temperature at a rate of 1  $\degree$ C/min, slowing down to 0.5  $\degree$ C/ min as the SMP was reached. The heating was continued until the fat column was raised. The temperature at which the fat column rose was reported as the SMP.

Solid Fat Content (%SFC) by Nuclear Magnetic Resonance (NMR)

The samples were melted and put into the sample tubes (10 mm o.d.  $\times$  75 mm length) up to a height of 3 cm. They were tempered at 70  $\degree$ C for 30 min, chilled at 0  $\degree$ C for 90 min, and kept at the desired temperatures in preequilibrated thermostated baths for 30 min prior to measurement. The measuring temperatures were 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, and 55 °C. The instrument used was a Bruker Minispec PC 120 pulsed NMR. The direct method was employed for the measurements.

# Results and Discussion

## Effect of Randomization

Interesterification not only rearranges the distribution of the fatty acids among the triacylglycerols of fats or mixtures of fats but also changes the fatty acid composition of the fats. A lot of discussions can be found in the literature regarding the incorporation of beneficial fatty acids into natural oils and fats. Most of them used an enzymatic route to alter the FAC of the original reactants. Konishi et al. [[29\]](#page-7-0) conducted a sodium methoxide-catalyzed ester interchange between soybean oil and methyl stearate in hexane at low reaction temperatures. They found that the stearic acid concentrations in TAG interesterified with methyl stearate was increased significantly in the presence of 10% (w/w) sodium methoxide. The reaction was carried out at 40  $^{\circ}$ C for 90 min. In 2003, Fajardo et al. [[30\]](#page-7-0) incorporated n-3 PUFA into palm oil by a lipase-catalyzed reaction. They successfully produced palm oil containing EPA and DHA which may be beneficial for food applications.

Successful interesterification is often monitored by color change. The oil turns to a reddish brown after a chemical catalyst is added [[31\]](#page-7-0). Chemical interesterification is normally carried out in excess time to ensure complete randomization. Figure 1 shows the effect of reaction time on the oleic content and the formation of free fatty acid (FFA) and diacylglycerol (DAG) in the interesterified oil. As the reaction time increased, the formation of FFA increased significantly. The increased FFA was accompanied by a lower oleic content and an increment in DAG content. The DAG increase from 5.3 to 13.1% after an hour of reaction. The increment of the DAG content was related to the formation of diacylglycerol ion from TAG during interesterification. However, the DAG content decreased to 10.3% at 90 min of reaction. At this stage, the DAG started to hydrolyse to form FFA and MAG. Hence, the FFA kept increasing with the reduction of DAG content.

Table [1](#page-4-0) shows the FAC of the oils before and after 30 min of randomization. The reaction has resulted in an increase of oleic content in the high oleic palm oil (HOPO). Palmitic acid had been reduced to nearly half of its original content. Stearic acid however had almost double the content in the composition as compared to the initial value. Approximately 30% of oleic acid was incorporated into the



Fig. 1 Effect of reaction time on oleic content and formation of free fatty acid (FFA) and diacylglycerol (DAG) in the interesterified oil

<span id="page-4-0"></span>Table 1 Fatty acid composition of oils before and after chemical interesterification

Fatty acids $(\%)$	RBD PO <sub>o</sub>	Methyl oleate	Mixture		<b>HOPO</b>
			Before	After	
$C12-0$	$0.2 \pm 0.0$	$0.0 \pm 0.0$	$0.1 \pm 0.0$	$0.2 \pm 0.0$	$0.2 \pm 0.0$
$C14-0$	$1.1 \pm 0.0$	$0.0 \pm 0.0$	$0.3 \pm 0.0$	$0.5 \pm 0.0$	$0.7 \pm 0.1$
$C16-0$	$35.7 \pm 0.4$	$0.3 \pm 0.0$	$8.8 \pm 1.3$	$16.4 \pm 1.1$	$20.3 \pm 1.8$
$C18-0$	$3.5 \pm 0.0$	$10.0 \pm 0.1$	$8.3 \pm 0.4$	$7.0 \pm 0.2$	$6.1 \pm 0.4$
$C18-1$	$45.4 \pm 0.2$	$71.1 \pm 0.1$	$65.2 \pm 0.9$	$59.5 \pm 0.9$	$56.7 \pm 1.3$
$C18-2$	$13.1 \pm 0.4$	$17.2 \pm 0.0$	$16.2 \pm 0.2$	$15.2 \pm 0.1$	$14.8 \pm 0.1$
$C18-3$	$0.3 \pm 0.0$	$0.4 \pm 0.0$	$0.4 \pm 0.0$	$0.3 \pm 0.0$	$0.3 \pm 0.0$
IV	$62.7 \pm 0.4$	$91.9 \pm 0.2$	$84.5 \pm 0.4$	$78.7 \pm 0.4$	$75.1 \pm 1.4$
<b>SFA</b>	$40.6 \pm 0.5$	$10.3 \pm 0.2$	$17.4 \pm 1.3$	$24.2 \pm 1.3$	$27.4 \pm 1.8$
<b>MUFA</b>	$45.4 \pm 0.2$	$71.1 \pm 0.1$	$65.2 \pm 0.9$	$59.5 \pm 0.9$	$56.7 \pm 1.3$
<b>PUFA</b>	$13.4 \pm 0.5$	$17.6 \pm 0.1$	$16.6 \pm 0.2$	$15.5 \pm 0.1$	$15.1 \pm 0.2$

Means of three determinations  $+$  standard deviation

RBD POo refined, bleached, deodorized palm olein, HOPO high oleic palm oil, IV iodine value, SFA saturated fatty acids, MUFA monounsaturated fatty acids, PUFA polyunsaturated fatty acids

HOPO after the interesterification reaction. The other fatty acids remained almost unchanged in composition. The increase of mono- and polyunsaturated fatty acids resulted in higher Iodine Value (IV) of the interesterified oil.

Table 2 illustrates the main TAGs of the oils before and after interesterification. The rearrangement of fatty acids caused by randomization resulted in significant changes in TAG composition. Triunsaturated (UUU) and diunsaturated–saturated (SUU) fatty acid containing TAGs such as OOO, OLO, OLL and SOO increased considerably after the reaction whereas the other SUU TAGs of PLO and POO experienced a reduction in composition. The descending pattern was also observed in the disaturatedunsaturated (SSU) TAGs namely PLP and POP. Generally, randomization had converted most of the SUU and SUS TAGs into UUU TAGs. Relatively, HOPO contained 230 and 450% higher OOO and OLO, respectively compared to that of RBD POo.

Randomization of refined, bleached and deodorized palm oil (RBD PO) as a substrate with MO resulted in an approximately similar finding. However, the incorporation of oleic acid in the interesterified oil was greater as compared to RBD POo as shown in Table [3](#page-5-0). The oleic content increased from 37.9 to 53.5%, which corresponds to an elevation of more than 41%. The changes of palmitic and stearic acids were comparable with randomization of RBD POo, where the former reduced into half of its composition while the latter had a double in composition. The IV of the interesterified oil was higher as compared to the starting RBD PO but still lower than that of the interesterified RBD POo. Alteration of TAG composition is presented in Table [4](#page-5-0). The UUU and SUU TAGs, namely OOO, OLO, PLO and POO regained their composition after

Table 2 Major triacylglycerols (TAGs) composition of oils before and after chemical interesterification

Triacylglycerols RBD POo		Mixture		<b>HOPO</b>
(%)		<b>Before</b>	After	
OLL.	$0.7 \pm 0.0$	$0.4 \pm 0.0$		$2.0 \pm 0.2$ 4.0 $\pm$ 0.2
<b>OLO</b>	$2.6 \pm 0.0$	$1.4 \pm 0.1$		$6.9 \pm 0.8$ 14.5 $\pm$ 0.6
PLO	$14.8 \pm 0.1$	$7.4 \pm 0.3$	$5.2 \pm 0.4$	$10.4 \pm 0.3$
PLP	$10.2 \pm 0.1$	$5.0 \pm 0.2$		$1.3 \pm 0.5$ $2.2 \pm 0.4$
000	$5.5 \pm 0.0$	$2.9 \pm 0.1$	$8.6 \pm 0.8$	$18.2 \pm 0.6$
POO	$30.6 \pm 0.1$	$15.3 \pm 0.5$	$10.3 \pm 0.8$	$20.3 \pm 0.7$
<b>POP</b>	$18.0 \pm 0.1$	$9.0 \pm 0.3$	$3.6 \pm 0.9$	$6.5 \pm 0.7$
SO <sub>O</sub>	$3.3 \pm 0.0$	$1.7 \pm 0.0$	$3.2 \pm 0.2$	$6.6 \pm 0.2$

Means of three determinations  $\pm$  standard deviation

P palmitic, S stearic, O oleic, L linoleic acid, RBD POo refined, bleached, deodorized palm olein, HOPO high oleic palm oil

randomization. The PLP, POP and PPP TAGs, which are the SUS and SSS TAGs shows a declining pattern.

The conversion of saturated into unsaturated rich TAGs could be improved by the amount of catalyst used as well as the ratio of the reactants. Konishi et al. [[29\]](#page-7-0) proved that 10% of the catalyst that was dispersed in hexane could incorporate more stearic acid in the interesterified oil as compared to 5.5% and below in sodium methoxide-catalyzed ester interchange between soybean oil and methyl stearate. The ratio of the stearic acid source (methyl stearate) to the oil was 4:1. However, excess catalyst would cause extra formation of soap and reduce the amount of the interesterified product. In a pilot plant and industrial productions, excess catalyst leads to a lot of losses.

Fatty acids $(\%)$	RBD PO	Methyl oleate	Mixture		<b>HOPO</b>
			Before	After	
$C12-0$	$0.2 \pm 0.0$	$0.1 \pm 0.0$	$0.1 \pm 0.0$	$0.2 \pm 0.0$	$0.2 \pm 0.0$
$C14-0$	$1.1 \pm 0.0$	$0.0 \pm 0.0$	$0.4 \pm 0.0$	$0.6 \pm 0.0$	$0.6 \pm 0.0$
$C16-0$	$45.7 \pm 0.0$	$0.4 \pm 0.0$	$13.8 \pm 0.0$	$22.9 \pm 0.0$	$23.2 \pm 0.0$
$C18-0$	$4.4 \pm 0.1$	$10.6 \pm 0.0$	$8.8 \pm 0.0$	$7.5 \pm 0.0$	$7.5 \pm 0.1$
$C18-1$	$37.9 \pm 0.0$	$69.4 \pm 0.0$	$60.0 \pm 0.1$	$53.8 \pm 0.0$	$53.5 \pm 0.0$
$C18-2$	$9.9 \pm 0.0$	$18.3 \pm 0.0$	$15.8 \pm 0.0$	$14.1 \pm 0.0$	$14.2 \pm 0.1$
$C18-3$	$0.2 \pm 0.0$	$0.4 \pm 0.0$	$0.4 \pm 0.0$	$0.3 \pm 0.0$	$0.3 \pm 0.0$
IV	$50.3 \pm 0.0$	$92.2 \pm 0.0$	$79.9 \pm 0.1$	$71.4 \pm 0.0$	$71.2 \pm 0.1$
<b>SFA</b>	$51.4 \pm 0.1$	$11.1 \pm 0.0$	$23.1 \pm 0.0$	$31.2 \pm 0.0$	$31.5 \pm 0.1$
<b>MUFA</b>	$37.9 \pm 0.0$	$69.4 \pm 0.0$	$60.0 \pm 0.1$	$53.8 \pm 0.0$	$53.5 \pm 0.0$
<b>PUFA</b>	$10.1 \pm 0.0$	$18.7 \pm 0.0$	$16.2 \pm 0.0$	$14.4 \pm 0.0$	$14.5 \pm 0.1$

<span id="page-5-0"></span>Table 3 Fatty acid composition of oils before and after chemical interesterification with RBD PO as a substrate

Means of two determinations ± standard deviation

RBD PO refined, bleached, deodorized palm oil, IV iodine value, SFA saturated fatty acids, MUFA monounsaturated fatty acids, PUFA polyunsaturated fatty acids

Table 4 Major triacylglycerols (TAGs) composition of oils before and after chemical interesterification with RBD PO as a substrate

Triacylglycerols RBD PO	Mixture		<b>HOPO</b>
	<b>Before</b>	After	
$1.8 \pm 0.1$	$0.9 \pm 0.0$	$6.7 \pm 0.1$	$12.4 \pm 0.1$
$9.9 \pm 0.1$	$5.1 \pm 0.0$		$6.4 \pm 0.1$ 12.1 $\pm$ 0.1
$9.5 \pm 0.1$	$5.0 \pm 0.1$	$1.7 \pm 0.1$	$3.1 \pm 0.0$
$4.2 \pm 0.0$	$2.2 \pm 0.0$	$8.6 \pm 0.1$	$16.1 \pm 0.1$
$21.5 \pm 0.1$	$11.2 \pm 0.1$	$12.5 \pm 0.1$	$23.5 \pm 0.0$
$28.7 \pm 0.1$	$15.0 \pm 0.0$	$5.2 \pm 0.0$	$9.9 \pm 0.0$
$5.6 \pm 0.0$	$2.9 \pm 0.0$	$0.7 \pm 0.1$	$1.3 \pm 0.2$
$2.6 \pm 0.1$		$3.4 \pm 0.0$	$6.4 \pm 0.1$
			$1.4 \pm 0.1$

Means of two determinations  $\pm$  standard deviation

P palmitic, S stearic, O oleic, L linoleic acid, RBD PO refined, bleached, deodorized palm oil, HOPO high oleic palm oil

## Dry Fractionation of Interesterified Product

During either single or double-step fractionation, more saturated fatty acids and triacylglycerols are gradually concentrated in the solid phase, leaving behind a more unsaturated liquid phase as the crystallization proceeds [\[32](#page-7-0)]. These fractions differ chemically and physically to the mother oil. Physico-chemical properties of HOPO and its fractionated products are presented in Table [5](#page-6-0).

Fractionation of HOPO segregated the saturated fatty acids to the solid fraction. The migration of palmitic and stearic acids to the solid fraction resulted in an enrichment of these fatty acids. The increment of oleic and linoleic acids in the liquid fraction was less significant as HOPO

was mostly in liquid form. Furthermore, the yield of the solid fraction was just 25%. As such, fractionation at 8  $^{\circ}$ C was only enhancing another 4 unit of oleic content in the liquid fraction. Lower fractionation temperature would increase the oleic content of the fraction. However, lower fractionation temperature would result in less olein yield. In general, the fractionation of HOPO at 8 $\degree$ C enhanced the palmitic and stearic content in the solid fraction. The enrichment of these fatty acids were accompanied with depletion of oleic and linoleic content. On the other hand, in liquid fraction, the enhancement of oleic and linoleic content resulted in a more unsaturated oil. The other fatty acids remained unchanged in composition.

The iodine value of the olein was higher but lower for the stearin as compared to the mother oil. HOPOo had an IV of 80.5 whereas 61.4 is the IV for the HOPS. It was noticed that the IV of the HOPS is almost identical to that of RBD POo (IV 62). This may be due to lower saturation of the interesterified stearin. It has almost similar composition of oleic and linoleic acid but lower amount of palmitic acid. Even though the FAC was almost similar, the physical property was totally different. HOPS was a solid at ambient temperature  $(25 °C)$  whereas RBD POo was in liquid form. Slip melting point (SMP) analysis showed a comparable value between HOPS and palm oil (PO). HOPS had an SMP of about 38  $\degree$ C while PO had an SMP ranging from 33 to 39  $\degree$ C. HOPS is therefore suitable to replace palm oil in some food applications such as in margarine and shortening formulations. Berger [\[33](#page-7-0)] reported that cake shortening should have a melting point of about 40  $\degree$ C. The solid fat profile of HOPS in comparison with PO is shown in Fig. [2.](#page-6-0) At  $0^{\circ}$ C, palm oil contained higher solid content than HOPS. Both fats melted

<span id="page-6-0"></span>Table 5 Physical and chemical properties of HOPO and its fractionated products

	<b>HOPO</b>	Dry fractionation	
		<b>HOPOo</b>	<b>HOPS</b>
Yield $(\%)$		75.4	24.6
$C12-0$	$0.2 \pm 0.0$	$0.2 \pm 0.0$	$0.2 \pm 0.0$
$C14-0$	$0.7 \pm 0.1$	$0.6 \pm 0.1$	$0.8 \pm 0.1$
$C16-0$	$20.3 \pm 1.8$	$17.3 \pm 1.3$	$29.5 \pm 1.4$
$C18-0$	$6.1 \pm 0.4$	$4.5 \pm 0.7$	$9.8 \pm 1.2$
$C18-1$	$56.7 \pm 1.3$	$60.5 \pm 0.9$	$46.9 \pm 0.3$
$C18-2$	$14.8 \pm 0.1$	$16.0 \pm 0.1$	$11.8 \pm 0.2$
$C18-3$	$0.3 \pm 0.0$	$0.3 \pm 0.1$	$0.2 \pm 0.1$
IV	$75.1 \pm 1.4$	$80.5 \pm 0.7$	$61.4 \pm 0.2$
<b>SFA</b>	$27.4 \pm 1.8$	$22.6 \pm 1.0$	$40.3 \pm 0.4$
<b>MUFA</b>	$56.7 \pm 1.3$	$60.5 \pm 0.9$	$46.9 \pm 0.3$
<b>PUFA</b>	$15.1 \pm 0.2$	$16.3 \pm 0.1$	$12.1 \pm 0.2$
SFA:MUFA:PUFA	0.5:1.0:0.3	0.4:1.0:0.3	0.9:1.0:0.3
Cloud point $(^{\circ}C)$		$-1.5 \pm 0.1$	
Slip melting point $(^{\circ}C)$			$38.4 \pm 0.1$

HOPOo high oleic palm olein, HOPS high oleic palm stearin, SFA saturated fatty acids, MUFA monounsaturated fatty acids, PUFA polyunsaturated fatty acids

completely at 45 $\degree$ C. It was noticed that the solid fat content (SFC) at 15 to 35  $\degree$ C for both fats is almost identical.

Fractionation of HOPO at  $8^{\circ}$ C further improved the cloud point of the resulting olein. HOPOo had a better cloud point (CP) of  $-1.5$  °C as compared to the CP of normal palm olein of around 13  $^{\circ}$ C. With a lower range of cloud points, the HOPOo is expected to pass the stringent cold stability test. Fractionation of HOPO at lower temperatures produced HOPOo with better cold stability and a steeper solid fat content of HOPS [[23\]](#page-7-0).

The chemical properties of interesterified RBD PO and its fractionated products are tabulated in Table 6. The findings were almost similar with the fractionation of



Fig. 2 Solid fat content of HOPS in comparison with RBD PO

Table 6 Chemical properties of HOPO and its fractionated products derived from RBD PO

	<b>HOPO</b>	Dry fractionation	
		<b>HOPOo</b>	<b>HOPS</b>
Yield $(\%)$		65.5	34.5
$C12-0$	$0.2 \pm 0.0$	$0.2 \pm 0.0$	$0.2 \pm 0.0$
$C14-0$	$0.6 \pm 0.0$	$0.6 \pm 0.0$	$0.7 \pm 0.0$
$C16-0$	$23.2 \pm 0.0$	$19.3 \pm 0.0$	$30.8 \pm 0.1$
$C18-0$	$7.5 \pm 0.1$	$5.9 \pm 0.0$	$10.4 \pm 0.0$
$C18-1$	$53.5 \pm 0.0$	$57.8 \pm 0.1$	$45.5 \pm 0.1$
$C18-2$	$14.2 \pm 0.1$	$15.5 \pm 0.0$	$11.5 \pm 0.1$
$C18-3$	$0.3 \pm 0.0$	$0.3 \pm 0.0$	$0.2 \pm 0.0$
IV	$71.2 \pm 0.1$	$77.2 \pm 0.0$	$59.5 \pm 0.1$
<b>SFA</b>	$31.5 \pm 0.1$	$26.0 \pm 0.0$	$42.1 \pm 0.1$
MUFA	$53.5 \pm 0.0$	$57.8 \pm 0.1$	$45.5 \pm 0.1$
<b>PUFA</b>	$14.5 \pm 0.1$	$15.8 \pm 0.0$	$11.7 \pm 0.1$

HOPOo high oleic palm olein, HOPS high oleic palm stearin, SFA saturated fatty acids, *MUFA* monounsaturated fatty acids, *PUFA* polyunsaturated fatty acids

interesterified RBD POo. As predicted, the saturated fatty acids namely palmitic and stearic were enriched in the solid fraction. However, the increment of the unsaturation of the liquid fraction was less significant as the interesterified oil is highly liquid. The olein yield is more than 65%. Relatively, randomization of RBD PO as a substrate gave a lower olein yield as compared to that of RBD POo. A lower IV (77.2) was also observed in the fractionated olein.

The oleic content of HOPOo is slightly lower than other high oleic oils, including olive oil. Generally, HOPOo has a comparable FAC with olive oil. The IV and oleic content of the oil could be further improved by lower fractionation temperatures.

An economic analysis of this work was carried out for better understanding and to enhance the commercialization process. Undoubtedly, the distillation stage is the most expensive step in the production of the high oleic palm oils. Assuming that palm olein is traded at RM 1,600 per tonne, the high oleic palm olein will cost approximately 2.25 times more than the normal olein. This value is however still below the price of high oleic sunflower oil currently traded in the market. The ester from this process can be recycled and sold as saturated ester. The high oleic palm stearin could also be sold at slightly higher price than normal palm stearin due to its enhanced oleic content.

#### Conclusions

Chemical interesterification of palm olein in the presence of methyl oleate followed by fractionation of interesterified

<span id="page-7-0"></span>product was able to increase the oleic content of the oil. By increasing the oleic acid, the physico-chemical properties of the resulting olein were improved as well. It has a better cloud point and is expected to pass the stringent cold stability test. The solid stearin had unique properties. The solid fat content was comparable to normal palm oil but it was totally solid at ambient temperature. Palm oil at the same condition is a semi solid. This large scale research had proven the capability of the pilot plant to produce such oils. Production of the products on a pilot scale gave the most realistic scenario for possible commercialization and industrial scale up.

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