

Glycerolysis-Interesterification of Palm Olein and Coconut Oil Blend using Two High-Shear Continuous Stirred Tank Reactors

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This study aimed to synthesize structured lipids containing high mono- and diacylglycerol by glycerolysis-interesterification of palm olein and coconut oil blend in two high-shear continuous stirred tank reactors in series. The result showed that various flow rates of 11 mL/min to 23 mL/min did not significantly increase mono- and diacylglycerol concentration, while at a flow rate of 26 mL/min only a low concentration of mono- and diacylglycerol was formed. However, a flow rate 20 mL/min and an agitating speed of 2000 rpm produced mono- and diacylglycerol concentration of 61.7% with the highest productivity of 2.1%/min and a triacylglycerol conversion of 64.6%. The slip melting point, melting point, hardness, emulsion capacity, and stability were 23.77 °C, 30 °C, 14.6 N, 65.15%, and 59.15%, respectively. The product's solid fat content at 25 °C was lower than cocoa butter. The product contained β' and β crystals, thus it can be applied as a cocoa butter substitute.

Keywords: Glycerolysis-interesterification, Continuous stirred tank reactor, Monoacylglycerol, Diacylglycerol, Palm olein, Coconut oil.

INTRODUCTION

Glycerolysis-interesterification is a method for modifying vegetable oils to obtain structured lipids (SLs) containing high mono- and diacylglycerol (MDAG). The reaction was performed between two types of oils and glycerol, according to¹. The glycerolysis-interesterification process was typically carried out at high temperatures, namely 200–240 °C^{2, 3}. However, the high temperature could result in undesirable by-products and affect the quality and stability of the products³. The way to produce a product with a high concentration of MDAG without the need to use high temperatures was to increase the agitating speed using a high-mixing rate in a high-shear reactor. An agitating speed of 2000 rpm with a high-shear reactor was used to produce a high concentration of MDAG⁴.

This process could be performed in various reactors, including packed bed reactor^{5–9}, slit-channel reactor¹⁰, stirred tank reactor with batch^{11, 12}, or continuous^{13–15} systems. In order to maximize the yield and quality of the product, it is necessary to choose the proper reactor.

Batch stirred tank reactor (BSTR) is a common glycerolysis-interesterification method. BSTR allows the glycerolysis-interesterification process to operate with high conversion yields, simplified reactor settings, and equipment maintenance¹⁶. However, the glycerolysis-interesterification process on a wide scale utilizing BSTR requires a huge reactor volume, resulting in high investment costs and the risk of batch-to-batch variance in product quality¹⁷. Therefore, BSTR is difficult to apply on an industrial scale.

Using a stirred tank reactor with a continuous system is an alternative for MDAG synthesis by glycerolysis-interesterification. A continuous stirred tank reactor (CSTR) combines a batch reactor and a fixed bed reactor in which reactants/materials are continually fed, and products are continuously produced¹⁶. CSTR operates with the requirement for a more significant amount of material and a rapid reaction speed. With the appropriate flow rate, it can achieve high yields¹⁸. CSTR also improves mass and heat transfer compared to BSTR, resulting

in greater process efficiency in less time¹¹. Moreover, CSTR is more cost-effective because this technology could reduce processing time¹⁹. However, a large reactor diameter was required to achieve the same reaction rate as a fixed-bed reactor¹⁶.

There are two alternatives for increasing productivity with CSTR. The first option is to increase the size of the reactor tank. The glycerolysis-interesterification process using CSTR instead of BSTR could produce high and constant yields of 2-MAG over time²⁰. However, the large volume of the reactor tank could cause stagnant zones, where no reactions occurred due to the reactor tank's size²¹. Furthermore, a large stirrer with a high agitating speed is required as the process conditions become more complex than BSTR and the energy consumption increases^{10, 14}.

Another alternative for increasing productivity is to increase the number of reactors of the same volume installed in series. The series reactor design can enhance productivity and reduce the time required to reach equilibrium¹⁵. Compared to a single CSTR reactor, employing three CSTR reactors put in series enhanced the yield of fatty acid methyl esters from 86% to 97%¹³.

One of the factors affecting the glycerolysis-interesterification of vegetable oil to produce high mono- and diacylglycerol is the flow rate. The flow rate is related to the material's residence time. The correct residence time will give the oil and glycerol sufficient time to react and form structured lipids. In addition, based on²², the highest MDAG content from palm oil-based fats required a residence time of 30 min. In another study by⁷, when the residence time was increased from 23 min to 123 min, the fatty acid methyl ester yield increased from 8.07 to 96.75%. In addition, based on research by¹³, increasing the reaction time from 30 min to 2.5 hours increased the yield of fatty acid methyl ester from 13% to 86%.

In addition to flow rate, agitating speed affects the glycerolysis-interesterification process. High agitating speeds reduced mass transfer resistance between the oil and water phases, as well as the size of the emulsion droplet and the material's viscosity^{6, 16}. Furthermore, the contact surface between the oil and water phases incre-

ased, resulting in a stable emulsion system²³. Increasing the agitating speed from 200 to 800 rpm increased the yield of fatty acid methyl esters⁷.

Glycerolysis-interesterification of vegetable oils was planned to the required product character. Research by¹ regarding the glycerolysis-interesterification process using a blend of Refined Bleached and Deodorized Palm Stearin (RBDPS) and Palm Olein produced an MDAG concentration of 35%. In addition, research by²³ regarding glycerolysis-interesterification using a blend of palm stearin and palm olein resulted in an MDAG concentration of 38.63%. Meanwhile, research by⁴ regarding the glycerolysis process using a palm stearin and palm olein blend using a high shear continuous stirred tank reactor produced an MDAG concentration of 60.36%. Thus, in this study, the glycerolysis-interesterification process was expected to produce an MDAG concentration of at least 60% with a low melting point, allowing them to form products with good plasticity properties that could be used as a shortening or cocoa butter substitute²⁴.

Research on the glycerolysis-interesterification process using a high-shear reactor had previously been studied by²⁵, where the glycerolysis-interesterification process used a high-shear reactor with agitating speed of 2000 rpm which resulted in an MDAG concentration of 40%. However, the process still uses a batch system, making planning for scale up more difficult. Meanwhile, research on glycerolysis-interesterification using a high-shear reactor with a continuous system has been studied by⁴. However, the glycerolysis-interesterification process still uses one reactor. Thus, the novelty in this research is that the glycerolysis-interesterification process uses two high-shear stirred tank reactors continuously to improve the mixing process so that the process productivity increases.

The objective of the study was to evaluate the flow rate and agitating speed in the second reactor in increasing the productivity of the glycerolysis-interesterification process of palm olein and coconut oil blend using two high-shear continuous stirred tank reactor (2 HS-CSTRs). The yield, slip melting point, melting point, hardness, emulsion capacity, emulsion stability, melting profile, solid fat content, and polymorphism were evaluated.

METHODS

Material

Palm olein was obtained from PT Sinar Mas Agro Resources and Technology Tbk (Jakarta, Indonesia), coconut oil was obtained from P.T. Barco (Jakarta, Indonesia), and glycerol was obtained from P&G Chemicals (Kuantan, Malaysia). NaOH, citric acid, NaCl, acetic acid, methanol, ethyl ethanol, coomassie blue, and hexane were obtained from Merck KGaA (Darmstadt, Germany).

Glycerolysis-interesterification of palm olein and coconut oil blend at various processing time

The glycerolysis-interesterification reaction was performed by mixing a palm olein:coconut oil ratio of 50:50²⁴ and an oil:glycerol ratio of 1:5 mol/mol²⁶ and 3% of NaOH²⁷ at various processing times with various residence times (15, 17, 20, 24, 29, and 36 min) at three cycles reaction. The glycerolysis-interesterification reac-

tion began by simultaneously flowing glycerol, NaOH, and oil using a peristaltic pump to the reactors at 120 °C. After the glycerolysis-interesterification reaction, a 20% (w/v) citric acid solution was added dropwise into the product until pH seven was reached; this aimed to stop the reaction. The product was washed with 1:1 (v/v) 5% (w/v) NaCl solution and centrifuged at 2000 rpm for 10 min to separate the product⁴.

Glycerolysis-interesterification of palm olein and coconut oil blend at various flow rate

The glycerolysis-interesterification reaction was performed by mixing a palm olein:coconut oil ratio of 50:50²⁴ and an oil:glycerol ratio of 1:5 mol/mol²⁶ and 3% of NaOH²⁷. The flow rate was adjusted according to predetermined variables (11, 14, 17, 20, 23, and 26 mL/min). After the material was reacted in the first reactor, the material flowed into the second reactor with the same reaction conditions as in the first reactor⁴.

Glycerolysis-interesterification of palm olein and coconut oil blend at various agitating speed in the second reactor

The glycerolysis-interesterification reaction was performed by mixing a palm olein:coconut oil ratio of 50:50²⁴ and an oil:glycerol ratio of 1:5 mol/mol²⁶ and 3% of NaOH²⁷. The glycerolysis-interesterification reaction began by simultaneously flowing glycerol, NaOH, and oil using a peristaltic pump to the first reactor. The material flow rate was adjusted according to the best flow rate. The agitating speed in the first reactor was 2000 rpm which was adjusted by an overhead stirrer. After the material was reacted in the first reactor, the material flowed into the second reactor with the predetermined agitating speed (1000, 1500, 2000, 2500, and 3000 rpm) and the same reaction conditions as in the first reactor. After the glycerolysis-interesterification reaction, a 20% (w/v) citric acid solution was added dropwise into the product until pH seven was reached; this aimed to stop the reaction. The product was washed with 1:1 (v/v) 5% (w/v) NaCl solution and centrifuged at 2000 rpm for 10 min to separate the product⁴.

Experimental design

The experimental design in this study was a one variable-at-a-time (OVAT) approach. The variables were flow rate (11, 14, 17, 20, 23, and 26 mL/min) and agitating speed in the second reactor (1000, 1500, 2000, 2500, 3000 rpm). After the glycerolysis-interesterification process, the melting points & slip melting points, hardness, emulsion capacity, emulsion stability, melting profile, solid fat content, and polymorphism were analyzed.

Analysis of Acylglycerols

Thin Layer Chromatography (TLC) analysis was carried out on plate G60 F254 with hexane:ethyl ethanol:acetic acid developer solution in a ratio of 80:20:2 (v/v/v)²⁸. The sample composition was scanned using Camag Automatic TLC Scanner III "dummy" S/N (1.14.16) with Camag WinCATS to determine the mono-, di-, and triacylglycerols in the samples⁴.

Characterization of Structured Lipids

Melting Point and Slip Melting Point

Slip melting point (SMP) analysis was carried out using The AOCS method Cc. 3.25 and melting point (MP) analysis was carried out using The AOCS method Cc. 1.25²⁹ using a capillary tube ($D=1$ mm).

Hardness

The hardness was analyzed using a Universal Testing Machine (ZwickiLine Z0.5 to Z5.0, Germany). The fats were stored at 5 °C and the hardness measurement was performed at 25 °C³⁰.

Emulsion Capacity and Stability

Homogenization was performed using Ultra Turax (Ika ultra-turrax® t25 digital, Germany) to determine emulsion capacity while heating and centrifugation (DLAB, DM0636, Beijing China), were performed to determine emulsion stability³¹.

Melting Profile and Solid Fat Content

A Differential Scanning Colorimeter (DSC) (Shimadzu DSC-60 Plus, Japan) was used to examine the melting profile and solid fat content. A 10 mg sample was weighed and closed in an aluminum cup, while an empty DSC cup was tightly closed as a control. The DSC instrument's temperature was programmed by raising it to 100 °C and holding it there for 10 min to erase the prior thermal history. The sample was cooled to -20 °C at a rate of 10 °C/min and kept there for 5 min. The sample was warmed at a rate of 5 °C/min to a temperature of 100 °C. SFC was estimated at various temperatures from DSC heating thermogram data with partial integration and corrected by melting energy into melting mass³².

Polymorphism

Short spacing on X-ray films was measured with Enraf Nonius model FR 592 (Delft, The Netherlands)³³. The instrument was equipped with a fine-focus copper X-ray tube (SmartLab, Australia) (x-ray 40 kV, 30 mA) with SC70 as a detector. The fat/oil samples were melted to 70 °C and tempered at 25 °C for 30 min. The diffraction pattern was measured at 2θ between 3–30° and a scan rate of 2 deg/min. The short spacing of the β' form is at 4.2 and 3.8 Å, while the β form is at 4.6 Å.

Statistical Analysis

All experiments were repeated three times. The data were analyzed by one-way analysis of variance, and Tukey's test was applied to detect the differences. P values < 0.05 were considered significant. The results were given as means \pm standard deviations.

RESULTS AND DISCUSSION

Effect of processing time on the concentration of Monoacylglycerol, Diacylglycerol, and Mono- and- Diacylglycerol

Synthesis of structured lipids from a palm olein and coconut oil blend using 2 HS-CSTRs was carried out for three reaction cycles to ensure the glycerolysis-interesterification process ran continuously and had already reached an equilibrium stage.

Increasing MAG, DAG, and MDAG concentrations were observed in Figure 1 at various flow rates and operation times. Flow rates of 11 mL/min (Fig. 1A) produced a constant concentration of MAG, DAG, and MDAG when the sample was out of the reactor. However, at flow rates of 14 mL/min to 23 mL/min, MAG and DAG increased and reached equilibrium after 10–50 min (Fig. 1B–1E). Meanwhile, the formation of MAG and DAG was low at a flow rate of 26 mL/min (Fig. 1F).

They are because the flow rate affected the residence time of the material in the reactor. A low flow rate with a specific reactor volume provided a long residence time. Long residence time caused more extended contact between oil and glycerol, so more MDAG concentrations were formed⁹. Furthermore, using two HS-CSTRs for the glycerolysis-interesterification process of an oil-glycerol mixture in a liquid-liquid phase results in a more stable flow of material than a solid-liquid mixture, which leads to the formation of MDAG more quickly^{13, 34}.

The degree of interesterification increased from 10 min to 40 min of reaction²². This is because alkaline catalysts generally work optimally within 10–40 min. Changes in the concentration of free fatty acids during the reaction cause changes in the concentration of MDAG. A strong base catalyst would gradually saponify free fatty acids, weakening the catalyst's performance over time²².

Although there were differences in the pattern of increasing concentrations formed during the glycerolysis-interesterification process at flow rates of 11 mL/min, the formation of MDAG at flow rates of 14 mL/min to 23 mL/min followed a continuous process pattern³⁵. At a flow rate of 11 mL/min, constant concentration of MAG, DAG, and MDAG were produced continuously since the initial overflow of glycerolysis-interesterification product from the reactors. The glycerolysis-interesterification process at a flow rate of 11 mL/min did not significantly ($P > 0.05$) increase TAG to MDAG conversion at increasing the operation time.

Two reactors in continuous processes cause continued material input and product output¹³. Intermediate products from the first reactor would move to the second reactor. Thus, the unconverted TAG would undergo a glycerolysis-interesterification reaction and be converted to MDAG. As a result, the resulting MDAG concentrations were higher than the initial sampling. Using two HS-CTSRs in series could boost continuous process productivity while decreasing the reaction time required to reach equilibrium¹⁵. Research on biodiesel production using CSTR, using three CSTRs in series can overcome yield limitations due to too wide residence time and increase yields from 85.6% to 97%¹³.

The continuous interesterification of a blend of coconut oil and palm olein produced varying levels of process productivity. Flow rates range from 11 mL/min to 23 mL/min provided a productivity range of 0.6 to 2.1%/min from the start of the interesterification process until equilibrium conditions are reached. A 20 mL/min flow rate achieved a maximum productivity of 2.1%/min. Using two CTSRs in series could increase continuous process productivity while decreasing the reaction time required to reach equilibrium¹².

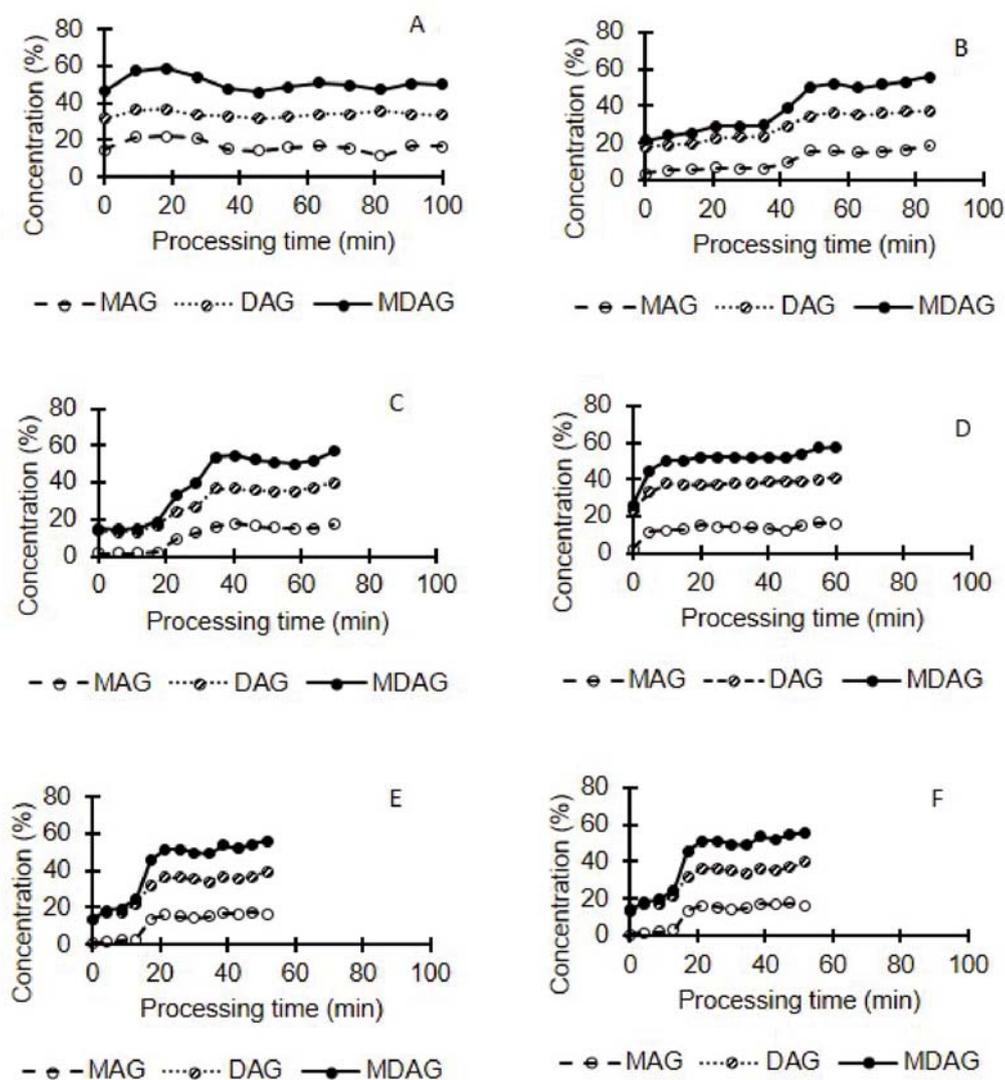


Figure 1. Effect of processing time on monoacylglycerol (MAG), diacylglycerol (DAG) and mono & diacylglycerol (MDAG) concentration. The glycerolysis-interesterification was carried out for three cycles reaction at 120 °C, agitating speed of 2000 rpm, palm olein:coconut oil ratio of 50:50 (w/w); an oil:glycerol ratio of 1:5 mol/mol; 3% of catalyst NaOH. T=0 min was determined after the samples started to overflow. (A):11 mL/min, (B):14 mL/min, (C):17 mL/min, (D):20 mL/min, (E):23 mL/min, (F):26 mL/min

Effect of flow rate on the concentration of Monoacylglycerol, Diacylglycerol, and Mono- and- Diacylglycerol

The concentrations of MAG, DAG, and MDAG were not significantly different ($P > 0.05$) at flow rates ranging from 11 mL/min to 23 mL/min, as shown in Figure 2. Furthermore, maximum TAG conversion was obtained at a flow rate of 20 mL/min, which was 1.17 times greater ($P < 0.05$) than the flow rates of 11 and 14 mL/min.

Flow rates ranging from 11 to 23 mL/min resulted in residence times ranging from 17 to 36 min. Low flow rates might increase MDAG concentration. It is due to the fact that as the residence time increased, the contact between the material and the catalyst increased, thus increasing the yield. A flow rate of 1.37 mL/min with a residence time of 27.9 min produced the highest yield in FAME production⁶.

Meanwhile, due to the short residence time of 15 min, the highest flow rate (26 mL/min) resulted in very low MAG and DAG concentrations. The shortest residence time for transesterification soybean oil yielded only

8.07%⁷. A high flow rate causes a short reaction time, preventing the optimal conversion of TAG to MDAG^{9,20}.

In the interesterification process of a blend of coconut oil and palm olein using 2 HS-CSTRs, the optimal flow rate of 20 mL/min achieved a high yield with the highest process productivity and TAG conversion. Therefore, a flow rate of 20 mL/min was used for the next research stage.

Effect of agitating speed in the second reactor on the concentration of Monoacylglycerol, Diacylglycerol, and Mono- and- Diacylglycerol

The MAG concentration significantly increased ($P < 0.05$) 1.44 times from the agitating speed of 1000 rpm to 2000 rpm, then decreased 0.19 times when the speed was increased to 3000 rpm (Fig. 3). Meanwhile, the DAG and MDAG concentration increased 1.15 times from agitating speed 1000 rpm to 2000 rpm but it was not significantly different ($P > 0.05$) at 2500 rpm and 3000 rpm.

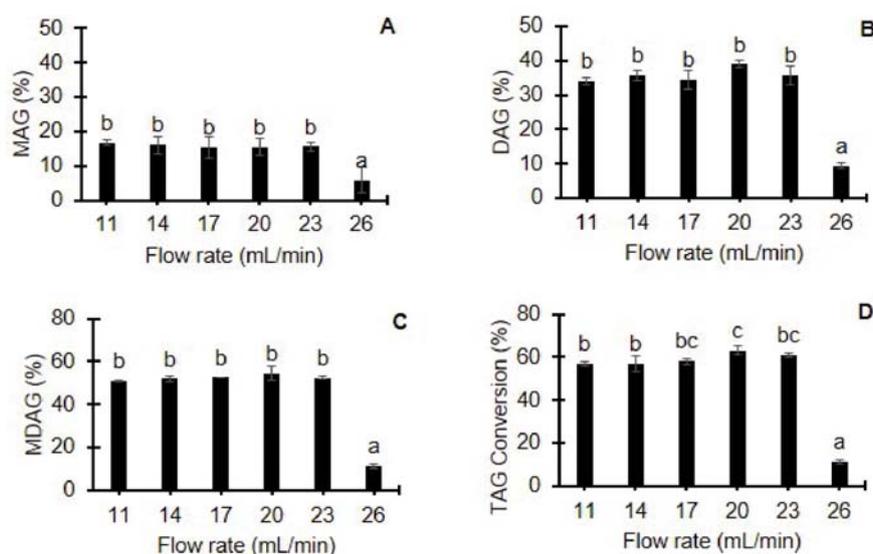


Figure 2. Effect of flow rate on monoacylglycerol (MAG) (A), diacylglycerol (DAG) (B), mono & diacylglycerol (MDAG) (C) concentration and TAG conversion (D). The Glycerolysis-interesterification was carried out for three cycles reaction at 120 °C, agitating speed of 2000 rpm, palm olein:coconut oil ratio of 50:50 (w/w); an oil:glycerol ratio of 1:5 mol/mol; 3% of catalyst NaOH. T = 0 min was determined after the samples started to overflow. Different letters indicated significantly different values ($P < 0.05$).

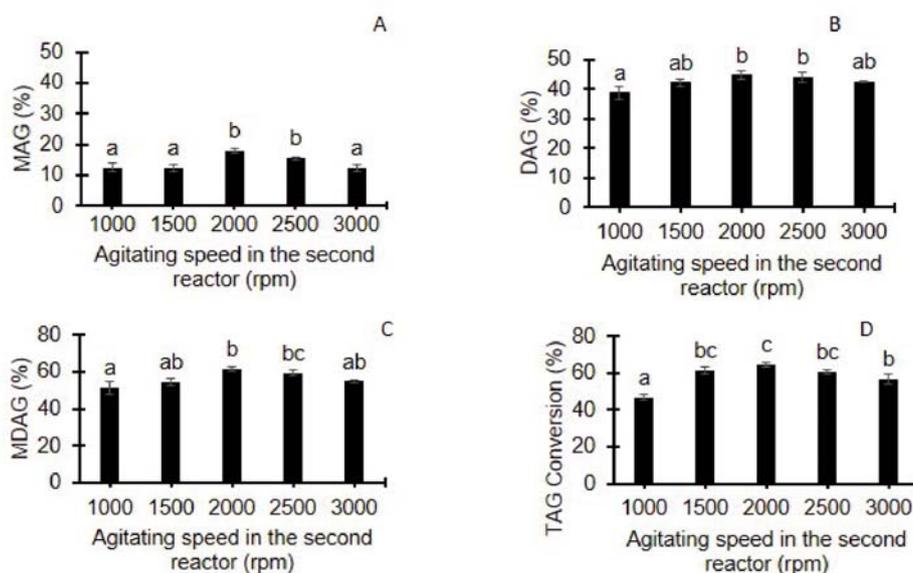


Figure 3. Effect of agitating speed in the second reactor on monoacylglycerol (MAG) (A), diacylglycerol (DAG) (B), mono & diacylglycerol (MDAG) (C) concentration and TAG conversion (D). The Glycerolysis-interesterification was carried out for three cycles reaction at 120 °C, flow rate of 20 mL/min, palm olein:coconut oil ratio of 50:50 (w/w); an oil:glycerol ratio of 1:5 mol/mol; 3% of catalyst NaOH. T = 0 min was determined after the samples started to overflow. Different letters indicated significantly different values ($P < 0.05$).

High TAG conversion supported the formation of products with high MAG and DAG concentrations. The TAG conversion showed a significant increase ($P < 0.05$) in the conversion percentage of 1.38 times from 1000 rpm to 2000 rpm, then it decreased significantly ($P < 0.05$) when the agitating speed was increased to 3000 rpm.

Because oil and glycerol are immiscible, a good agitating process is required so that the glycerolysis-interesterification process can produce high yields. High agitating speed reduces the barrier layer between the two phases, lowering mass transfer resistance⁷. Furthermore, in the continuous glycerolysis-interesterification process, the reactants (oil and glycerol with the help of a catalyst) go through a continuous heating and mass transfer process, increasing the reaction rate and process productivity³⁴.

A high agitating speed could reduce emulsion droplet size and increase the contact surface area between the water and oil phases, forming a good emulsion system²³. Furthermore, the high temperature (120 °C) reduced the material's viscosity, increasing the glycerolysis-interesterification reaction's yield¹⁶.

Thus, because of the highest MDAG concentration and TAG conversion, an agitating speed of 2000 rpm was chosen in the second reactor for later characterization.

Characterization of Structured Lipids

The yield of glycerolysis-interesterification

The initial DAG concentration was 12.66% (Table 1). At flow rate of 20 mL/min and an agitating speed of

Table 1. Characterization of Structured Lipids

Parameters	Palm Olein	Coconut Oil	PO-CO blend	Structured Lipids	Control Cocoa Butter
Monoacylglycerol (%)	nd	nd	nd	17.9 ± 0.6	
Diacylglycerol (%)	17.9	3.9	12.7 ± 0.4	44.7 ± 1.4	
Triacylglycerol (%)	82.1	96.1	87.7 ± 0.4	35.4 ± 1.2	
Slip melting point (°C)	nd	nd	18.6 ± 0.1	23.7 ± 0.4	25 35 ⁴⁸
Melting point (°C)	nd	nd	23.9 ± 0.1	30.0 ± 0.1	27.5 38.1 ⁴⁹
Hardness (N)	nd	nd	nd	14.6 ± 0.3	13 ³⁰ –15.6 ⁵⁰
Emulsion capacity (%)	nd	nd	34.9 ± 0.1	65.2 ± 0.2	
Emulsion stability (%)	nd	nd	nd	59.2 ± 1.2	

The results were given as means. nd: not defined. PO: palm olein, CO: coconut oil.

2000 rpm, the concentrations of MAG and DAG increased by 17.9 and 3.5%, respectively. It produced a TAG conversion rate of 64.63%. During the glycerolysis-interesterification process, the ester bonds in glycerol will break and randomly bind to fatty acids where 2 mol of glycerol interacts with 1 mol of TAG to produce 3 mol of MAG^{22, 27}. The glycerolysis-interesterification process with this flow rate had a residence time of 20 min. Therefore, it can be concluded that the residence time of 20 min produced products with high concentrations of MAG and DAG.

Slip melting point and melting point

The melting point was one of the parameters that could be used to determine the character of oil and its derivative products, which could further increase its application in the food sector³⁶. Some of its applications are margarine, shortening, and spread.

After glycerolysis-interesterification, the slip melting point and melting point of MDAG concentrations increased by 1.27 times and 1.25 times compared to palm olein and coconut oil blends, respectively (Table 1). The increase in melting point was related to the high MDAG concentration. MDAG has a higher melting point than TAG^{23, 37}. The higher melting point of MDAG is caused by the hydrogen bonds in the MDAG structure which are more difficult to break, so it takes more energy to melt the product³⁸.

The slip melting point of MDAG concentrations was lower than that of the interested product from virgin coconut oil and palm olein blend which produced a slip melting point in the range of 28.6–36.1 °C²⁴.

The melting point was the temperature when the fat completely melted and became clear in the capillary tube. Fat's melting point was affected by the degree of unsaturation³⁶. The higher the saturated fatty acid, the higher the melting point. Oleic fatty acid (C18:1) and palmitic fatty acid (C16:0) were the dominant fatty acids in palm olein, with a presentation of 41.7 and 42%, meanwhile, coconut oil contained dominant fatty acids in the form of medium-chain saturated fatty acids such as lauric acid (C12:0) of 49.5%³⁶. Therefore, the palm olein and coconut oil blend contained higher saturated fatty acids than unsaturated fatty acids where the saturated fatty acid content of a mixture of virgin coconut oil and palm olein was two times higher than the unsaturated fatty acids²⁴.

MDAG concentrations with low melting points provided good plasticity and spreadability and it could further improve the product's functional properties³⁹. One of its applications was as a shortening because this product could melt directly in the mouth without causing a waxy

sensation⁴⁰. The MDAG interesterified from palm olein and coconut oil blend could also be applied as cocoa butter replacer because its melting point was within the melting point range of cocoa butter.

The hardness

The product's hardness was 14.6 N, which was produced by an increase in the product's melting point and the concentration of MDAG (Table 1). The higher the concentration of MDAG in a product, the higher its melting point, which impacts the texture of the final hardness. A rise in the melting point of MDAG increases the hardness²³. Hardness decreased as a function of temperature⁴⁰. The greater temperature caused crystals to melt, resulting in a weakened network structure and the formation of fat plasticity. The product's hardness was within the range of the hardness texture of cocoa butter. This indicated that the interesterified product derived from a blend of coconut oil and palm olein could substitute cocoa butter in chocolate goods.

The emulsion capacity and stability

The glycerolysis-interesterification process could provide emulsification capabilities to the product. The emulsion capacity increased 1.86 times after glycerolysis-interesterification with stability of 59.15% (Table 1). Emulsion capacity was affected by the high concentration of MDAG in the product. Interesterified products containing more than 21% polar fractions (MAG and DAG) could provide good emulsification characteristics in the product, as well as produce high stability⁴¹. An emulsion capacity is increased up to 1.56 times after glycerolysis-interesterification²³.

Melting profile

The Differential Scanning Colorimeter (DSC) method was used to examine the melting profile of the MDAG product. The melting profile was obtained from the interesterified products at a flow rate of 15.75 mL/min and an agitating speed of 2707 rpm. The MDAG product has an onset temperature of 16.7 °C and an endset temperature of 31.42 °C with a melting point of 28.4 °C (Fig. 4). The results were in accordance with the melting point analysis using a capillary tube where the melting point of the MDAG product was 28.5 °C. However, the melting profile differs from the cocoa butter melting profile which has T_{onset} of 30.2 °C and T_{endset} of 36.1 °C⁴².

Solid fat content

The solid fat content was obtained from the interesterified products at a flow rate of 15.75 mL/min and an agitating speed of 2707 rpm. Over a temperature range

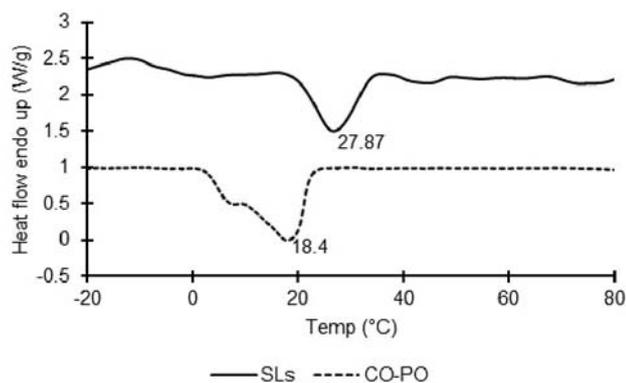


Figure 4. Melting profile of mono & diacylglycerol (MDAG) and coconut oil & palm olein blend. The glycerolysis-interesterification was carried out for three cycles reaction at 120 °C, flow rate of 15.75 mL/min, agitating speed of 2707 rpm, palm olein:coconut oil ratio of 50:50 (w/w); an oil:glycerol ratio of 1:5 mol/mol; 3% of catalyst NaOH

of -2 °C to 28.6 °C, the solid fat content of MDAG products decreased gradually (Fig. 5). At 20 and 25 °C, the solid fat contents were 28.9 and 11.9%, respectively, and it completely melted at 28.6 °C. So, there was no solid fat detected at above body temperature. The low melting temperature is because the raw material for MDAG products is a blend of coconut oil and palm olein, which is liquid at room temperature. The solid fat content of the oil blend at 15 °C was 18.4%, and the fat crystals completely melted at 18 °C. The solid fat contents of MDAG from virgin coconut oil and palm olein at 20 °C were 27.75%²⁴.

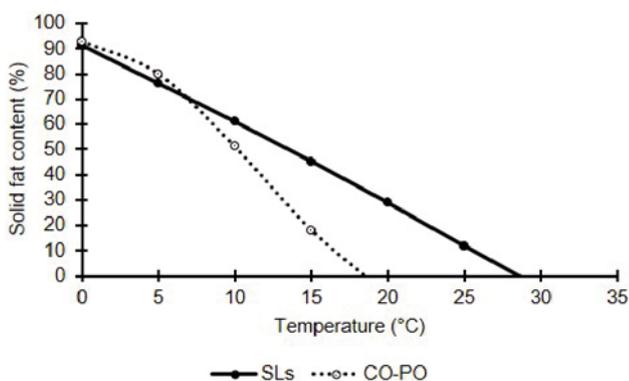


Figure 5. Solid fat content of mono & diacylglycerol (MDAG) and coconut oil & palm olein blend. The glycerolysis-interesterification was carried out for three cycles reaction at 120 °C, flow rate of 15.75 mL/min, agitating speed of 2707 rpm, palm olein:coconut oil ratio of 50:50 (w/w); an oil:glycerol ratio of 1:5 mol/mol; 3% of catalyst NaOH

Unfortunately, according to⁴³, the solid fat content of MDAG interesterified from palm olein and coconut oil blend was lower than cocoa butter, which still contained 73% at 20 °C and 4.2% at 35 °C. According to⁴³, the solid fat content of cocoa butter at temperatures ranging from 25 to 30 °C indicates the hardness of the fat and the occurrence of fat heat resistance, and solid fat content greater than 50% at 25 °C exhibited good melting properties and adequate snap at room temperature. Meanwhile, according to^{44,45}, temperatures above 37 °C

(above body temperature) can cause a waxy mouthfeel sensation.

Polymorphism

The x-ray diffraction was obtained from the interesterified products at flow rate of 15.75 mL/min and an agitating speed of 2707 rpm. Figure 6 shows X-ray diffraction of MDAG product with three diffraction peaks at 3.96, 4.35, and 4.55 Å. The intensity of d-spacings at 4.35 and 4.55 Å was not significantly different. According to the results, the MDAG product of a blend of coconut oil and palm olein had two crystal forms, β' and β . An increase in concentrations of MAG and DAG can lead to the formation of β' and β crystals with d-spacings of 4.6 and 3.9 Å^{44,45}. Glycerolysis of hydrogenated corn oil to MAG changed the crystal type β' crystal to β crystal³⁷. β' crystals typically have two strong d-spacings at 3.8 and 4.2 Å, whereas β crystals have one strong d-spacing at 4.6 Å and one weak d-spacing at 3.8 Å^{45,46}.

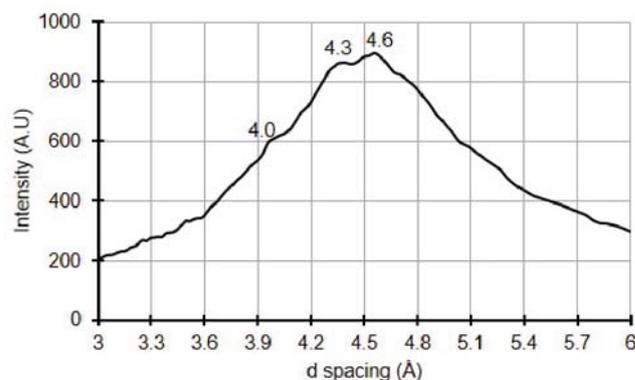


Figure 6. Polymorphism of mono & diacylglycerol (MDAG) and coconut oil & palm olein blend. The glycerolysis-interesterification was carried out for three cycles reaction at 120 °C, flow rate of 15.75 mL/min, agitating speed of 2707 rpm, palm olein:coconut oil ratio of 50:50 (w/w); an oil:glycerol ratio of 1:5 mol/mol; 3% of catalyst NaOH

The MDAG product from the PO-CO blend consisted of β' crystals agrees with the commercial CBR and CBS⁴⁶ with two d-spacings of 4.24 and 3.74. Furthermore, the oil blend contains a high level of palmitic acid (24.6–36.5%), which increases the tendency of β' crystal formation, which is ideal for the production of shortening and margarine²⁴. In the meantime, the preferred crystal form for cocoa butter is β crystals in form V, as these crystals have a fast melting profile in the mouth and are less likely to form blooms during the storage process⁴⁷.

CONCLUSION

Interesterification of a coconut oil and palm olein blend using two high-shear continuous stirred tank reactors could increase the productivity of the glycerolysis-interesterification process. The flow rate and agitating speed in the second reactor affected the glycerolysis-interesterification process. The use of flow rates is related to the material's residence time in the reactor. The slower the flow rate, the higher the reaction time of the material, so the concentration of MDAG was also higher. While the agitating speed is related to the emulsion system. The higher the agitating speed, the surface

area which contact between water and oil increased and improved the mixing process.

Using a flow rate of 11 to 23 mL/min resulted in insignificant MDAG concentrations, while at a flow rate of 26 mL/min only a small concentration of MDAG was formed. A flow rate of 20 mL/min and an agitating speed of 2000 rpm produced a MDAG concentration of 61.6% with the highest productivity of 2.1%/min and a TAG conversion of 64.6%. Increasing the agitating speed to 3000 rpm did not significantly increase the yield. MAG and DAG concentrations were $17.9 \pm 0.6\%$ and 44.7 ± 1.4 , while the slip melting point, melting point, hardness, emulsion capacity, and stability were 23.77 ± 0.4 °C, 30 ± 0.1 °C, 14.6 ± 0.32 N, $65.15 \pm 0.21\%$, and $59.15 \pm 1.2\%$, respectively. The melting point and hardness were within the range of cocoa butter but the solid fat content of the MDAG product at 25 °C was lower than that of cocoa butter due to the low melting point of coconut oil and palm olein. The MDAG product contains β and β' crystals with three diffraction peaks at 3.96, 4.35 and 4.55 Å. The results implied that the MDAG produced from a palm olein and coconut oil blend using two high-shear continuous stirred tank reactors can be applied as cocoa butter substitute.

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