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Interesterification Process Between Palm Oil Stearin Fraction and Yellow Pumpkin Seed Oil to Produce *Cocoa Butter Substitute*

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ABSTRACT

Interesterification process catalyzed with sodium methoxide has been used to produce *Cocoa Butter Substitutes* (CBS) from palm stearin fraction and yellow pumpkin seed oil. Time reaction of interesterification shows strong impact to the CBS characteristics i.e. melting point and symmetrical triacylglycerols composition. Interesterification reaction causes the decreasing of melting point from 59 ^{0}C (as stearin fraction) to 37.16 ^{0}C (as CBS) with 2 % catalyst. Analyzeing yellow pumpkin seed oil using FT-IR gives its performance of peak in 3007 which indicates that there are long chains C-H SP2 (C=C) and this is supported by the data of absorption peak at 907 wave numbers. This peak shows the yellow pumpkin seed oil contains unsaturated fatty acid composition. Meanwhile, from the FT-IR analysis, stearin oil does not find 3000s wave numbers specific to C-H SP2 from unsaturated bonds of aliphatic ester chains. However, from FT-IR result of interesterification's product, CBS, the performance of peak in 3006 appears. It indicates that there are unsaturated fatty acid chains which have been substituted to the gliserol. Symmetric triacylglycerols composition of interesterification's product, CBS, which is produced in 8 hours catalysed process consist of palmitic-oleic-palmitic (POP) 32.26 %, palmitic-oleic-stearic (POS) 5.24 %, stearic-oleic-stearic (SOS) 5.17 %.

Keywords: cocoa butter substitutes, catalyst, stearin oil, interesterification, sodium methoxide, yellow pumpkin seed oil

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INTRODUCTION

Cocoa butter (CB) is a fat with a unique physicochemical characteristics, CB completely melts in the human mouth with the creamy texture and a cool sensation but hardness at room temperature (Gunstone, 2002). CB's physicochemical characteristics are caused by its composition of triacylglycerols which is contain almost 80% dominated by three symetric triacylglycerols (saturated-monounsaturated-saturated). The symmetric triacylglycerols (TAGs) in CB consist of 2-oleolyl-1-palmitoyl-3-stearoyl-glycerol (POS) 36-42%, 2-oleolyl-1,3-disrearoyl-glycerol (SOS) 23-29% and 2-oleolyl-1,3-dipalmitoyl-glycerol (POP) 13-19% (Wainwright, 1996). The fatty acid composition in CB generally consists of 26% palmitic acid, 36% stearic acid, 33% oleic acid and 3% linoleic acid, but the composition is usually varied (Owusu-Ansah, 1994). CB has a range of melting points 15 - 36^{0}C (Huyghebaert, 1971). Producing chocolate from cocoa butter is a high cost process. The use of CB is also limited because of its erratic supply and variability in quality. Due to the uncertain supply and price increasing of cocoa butter drive the manufacturers to seek raw materials alternatives for Chocolate Industry and its products (Depoortere, 2011). One type of

Cocoa Butter Alternative (CBA) is Cocoa Butter Substitutes (CBS). CBS has no similar chemical properties to CB but some of its physical properties have similarities to CB and in small ratios can be compatible with CB (Zoumas et al, 1979). One of the methods to produce CBS is through chemical interesterification. Interesterification involves of redistribution and interchange of fatty acids in triglycerides. Chemical interesterification is known as a random interesterification (Young et al, 1994).

Chemical interesterification of various tea seed oil mixtures with NaOH catalyst produces Cocoa Butter Replacer (CBR) with melting points 28 - 31° C (Zarringhalami et al., 2012). Interesterification with an enzyme catalyst from a mixture of mango seed oil and CB in various ratios produces CBS which has a CB-like characteristic (Momeny, 2013). Interesterification process of Palm Oil using Carica Papaya Lipase catalyst gives the CBE with melting point of 37 - 39° C (Pinyaphong, 2009). Palm oil mid fraction and mango seeds oil are used to produce CBE with melting point 32 - 40^0C (Kaphueakngam, 2009). Interesterification of palm oil mixture gives the increasing of POS and SOS concentrations (the main triacylglycerols in CB) in CBE product which initially accounted for 2.6% and 0.5% to 14.6% and 6.9% (Soekopitojo, 2008). Acidolysis with lipase catalyst from the Palm oil mid fraction and palmitate and stearate fatty acid mixture produces CBE with melting point 31.6° C and the triglyceride composition comprised 30.7% POP, 40.1% POS, 9% POO, 14.5% SOS and 5.7% SOO (Mohamed, 2013)

The aim of this study is to produce CBS by interesterifying stearin oil and yellow pumpkin seed oil using chemical catalyst i.e. sodium methoxide and then characterizes the CBS product. Refinery process of palm oil produce two fractions: Refined Bleached Deodorized Palm Olein/RBD Palm Olein used as cooking oil and Refined Bleached Deodorized Palm Stearin/RBDPS. RBDPS is used as stearin oil in this study. Stearin oil with the aid of the catalyst undergoes redistribution and interchange (interesterification reaction) by adding pumpkin seed oil which is also rich with oleic, stearic and palmitic acid. Stearin oil is more dominant as a source of stearic and palmitic acid while pumpkin seed oil is more dominant as a source of oleic acid. Using both of stearin oil and pumpkin seed oil and applying a catalyzed reaction system, it is expected that the oil will undergo redistribution and interchange of fatty acids in order to alter the physical characteristics of the oil.

MATERIALS AND METHODS

Materials: Refined Bleached Deodorized Palm Stearin (RBDPS), obtained from refinery process of palm oil used as stearin oil. Pumpkin seed oil is obtained from extraction of pumpkin seeds. The catalyst used is sodium methoxide available in powder form. The solid-shaped citrate acid is used as the inactivation of interesterification reactions.

Extraction of pumpkin seed oil: Pumpkin seed oil is extracted from the pumpkin seed by extraction method using hexane solvent. The melting point, composition with Gas Cromatography (GC) of pumpkin seed oil, and functional group analysis with FT-IR are analyzed.

Interesterification of stearin oil and pumpkin seed oil: Stearin oil and pumpkin seeds oil are mixed with various ratios (1:2, 1:1 and 2:1). The oil mixture is heated to 70° C. The sodium methoxide catalyst is added to the raw material by variation of percentage to the raw material (2% and 4%). The reaction is carried out at 70° C by varying the reaction time (4.6 and 8 hours). And the result is characterized into melting point, triglyceride composition with GC, and functional group with FT-IR.

RESULTS AND DISCUSSION

Yellow pumpkin seed oil: FT-IR analysis of pumpkin seed oil is shown on figure 1. Specific peak for aliphatic ester (long chain) at 1743.07 wave number indicates the ester absorption peak C = O, whereas 1159.17 wave number indicates a C-O-C absorption peak. Wave numbers 2922 and 2853 indicate a long-chain absorption of CH2 (C-H SP3) and this is supported by absorption at 1460 wave number. While the 3007 wave number indicates the presence of CH SP2 (C = C) of long chains which is supported by the absorption peak in 907. These show oil composition comprises an unsaturated fatty acid structure. While the 720 wave number is the peak absorption of aliphatic chain (CH2)n.

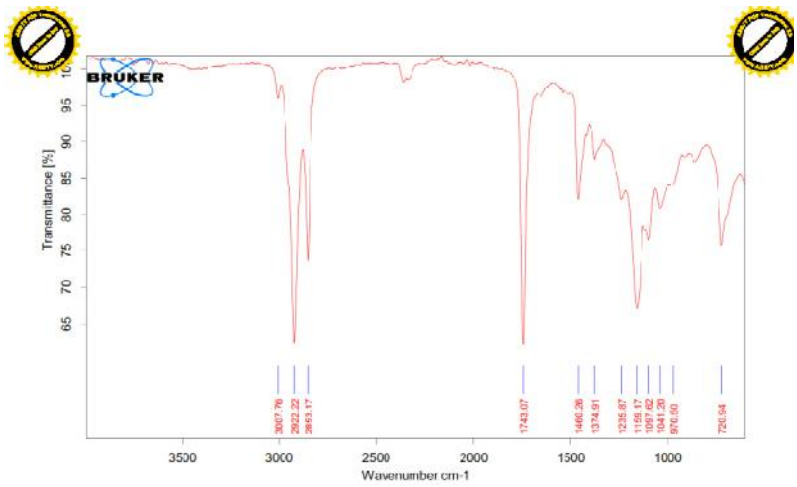

Figure 1. FT-IR Analysis of Pumpkin Seed Oil

Composition of POP and POS symmetric triglyceride is not found in pumpkin seed oil and there is SOS as much as 9,24%. The highest triglyceride composition in pumpkin seed oil

is PLO of 25.44%. Pumpkin seed oil is dominated by unsaturated fatty acids. The triacylglycerols composition is shown in Table 1.

Table 1. Triacylglycerols Composition of Pumpkin Seed Oil

Triacylglycerols	Units	Test Results
Palmitic-Linoleic-Oleic (PLO)	%	25,44
Palmitic-Oleic-Oleic (POO)	%	10,04
Stearic-Oleic-Stearic (SOS)	%	9,24
Stearic-Oleic-Oleic (SOO)	%	10,39
Oleic-Linoleic-Oleic (OLO)	%	19,95
Oleic-Oleic-Oleic (OOO)	%	15,98

Stearin oil: Stearin oil/RBDPS used in this study is the result of CPO Refinery Process. RBDPS is a palm oil fraction rich in saturated triglycerides. RBDPS is analyzed with FT-IR and shown in figure 2. The wave number of the RBDPS absorption peak shows the same thing as the pumpkin seed oil, the basic thing that distinguishes only the weak wave of 3000s wave numbers refers to C-H SP2 for unsaturated bonds of aliphatic ester chains..

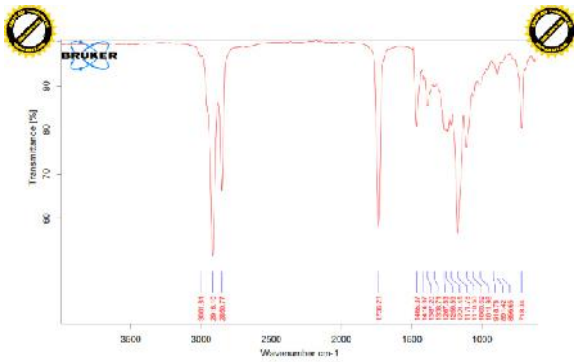

Figure 2. FT-IR Analysis of Stearin Oil /RBDPS

The symmetric triacylglycerols composition in RBDPS consists of POP (54,05%), POS (7,65%) and SOS (1,53%). The triacylglycerols composition is shown in Table 2. The highest triglyceride composition on RBDPS used in this study is POP of 54.05%. The RBDPS used in this study has a melting point of 59^{o}C

Table 2. Triacylglycerols Composition of RBDPS

Triacylglycerols	Unit	Test Result
Palmitic-Oleic-Palmitic (POP)	%	54,05
Palmitic-Linoleic-Oleic (PLO)	%	2,30
Palmitic-Palmitic-Palmitic (PPP)	%	4,66
Palmitic-Oleic-Stearic (POS)	%	7,65
Palmitic-Oleic-Oleic (POO)	%	25,1
Stearic-Oleic-Stearic (SOS)	%	1,53
Stearic-Oleic-Oleic (SOO)	%	5,49

Interesterification with sodium methoxide catalyst, variation ratio of stearin oil and pumpkin seed oil composition: Interesterification with variation of the composition ratio Stearin - Pumpkin Seed Oil are carried out under the same reaction conditions i.e. at temperature 70° C, for 4 hours and with 2% of sodium methoxide (Table 3).

Table 3. CBS from Interesterified Oil Blends: Stearin – Pumpkin Seed Oil

No	Oil Ratio In Raw Material	Variables			Melting Point (^oC)
		Catalyst Percentage (%)	Temperature Reaction (^oC)	Time Reaction (hour)	
1	1 : 2	2	70	4	55,2
2	1 : 1	2	70	4	55,4
3	2 : 1	2	70	4	55,7

Based on the melting point test, the result of triacylglycerols which is 55^0C is still close to the stearin oil melting point (59^0C). The triglyceride melting point which is produced from the interesterification reaction is higher than the Cocoa Butter melting point. Triacylglycerols from interesterification with oil ratio 1: 2 and 2: 1 are shown on Table 4. The dominant symmetric TG on the 2: 1 oil ratio is POP but at the 1: 2 ratio no SOS symmetric triglycerides are found. There is a change in triglyceride composition when compared to the triglyceride composition of RBDPS, but it is still dominated by POP triglycerides.

Table 4. Triacylglycerols Composition on Various Oil Blends Ratio

No	TAGs	Test Results (%)			
		Stearin Oil	Pumpkin Seed Oil	Ratio 2:1	Ratio 1:2
1	PPP	4,66	-	8,12	4,35
2	POP	54,05	-	66,0	47,99
3	PLP	-	-	0,87	-
4	POS	7,65	-	10,50	8,06
5	POO	25,1	10,04	12,78	22,89
6	SOS	1,53	9,24	0,53	-
7	SOO	5,49	10,39	0,62	3,57
8	OOO	-	15,98	0,57	6,8
9	PLO	2,3	25,44		3,84
10	OLO	-	19,95		2,52

Variation percentage of sodium methoxide catalyst: The result of interesterification products triacylglycerols with 40^OC on the melting point. Using 2% and 4% catalysts have no significant effect to the melting point of CBS. CBS which is produced in 6 hours reaction time and at temperature is 70^0C is able to obtain CBS with a melting point of 40^0C (Table 5).

Table 5. Data for Interesterification Process with Various Percentage of Sodium Methoxide Catalyst

No	Oil Ratio In Raw Material	Variables			Melting Point (^oC)
		Catalyst Percentage (%)	Temperature Reaction (^oC)	Time Reaction (hour)	
1	1 : 2	2	70	6	40,0
2	1 : 2	4	70	6	40,0

Triacylglycerols composition consist of palmitic – oleic - palmitic (POP) 53.91%, palmitic – oleic - stearic (POS) 8.96%, stearic - oleic - stearic (SOS) 0.88%. The symmetric triacylglycerols of POS, SOS, POP found on CBS from interesterification reaction is still dominated by POP 53,91%, while the percentage of POS and SOS content is still small.

Table 6. Triacylglycerols Composition on CBS Product from Interesterification with 4% Catalyst

No	TAGs	Test Results (%)		Catalyst 4%
		Stearin Oil	Pumpkin Seed Oil	
1	PPP	4,66	-	5,26
2	POP	54,05	-	53,91
3	PLP	-	-	-
4	POS	7,65	-	8,96
5	POO	25,1	10,04	25,30
6	SOS	1,53	9,24	0,88
7	SOO	5,49	10,39	3,99
8	OOO	-	15,98	-
9	PLO	2,3	25,44	1,70
10	OLO	-	19,95	

Variation of reaction time: Interesterification reactions are varied for 4, 6 and 8 hours and the results are shown in table 7. Reaction time greatly affects the melting point of triglycerides produced. The lowest CBs melting point of 37.16 ° C is obtained at 8 hours reaction time.

Table 7. Interesterification Reaction Data with Variation of Reaction Time

No	Oil Ratio In Raw Material	Variables			Melting Point (^oC)
		Catalyst Percentage (%)	Temperature Reaction (^oC)	Time Reaction (hour)	
1	1 : 2	2	70	4	55,2
2	1 : 2	2	70	6	40,0
3	1 : 2	2	70	8	37,16

The result of FT-IR analysis of the oil produced in 8 hours reaction time is shown on Figure 3. From the 8 hours reaction time found the 3006 wave number, this indicates that there are unsaturated chain substituted on glycerol.

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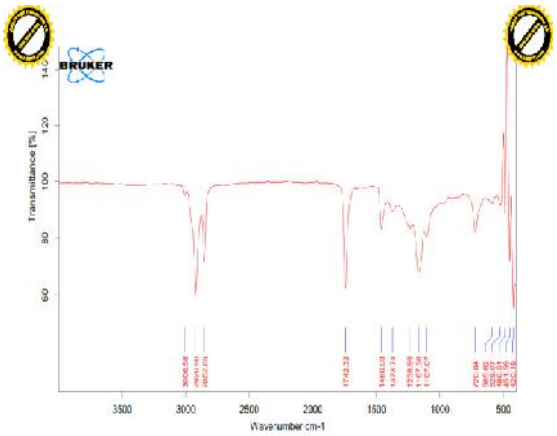

Figure 3. FT-IR Analysis on CBS which is produced in 8 Hours Reaction Time

The content of SOS on CBS has increased compared to the results obtained from variation of oil composition in raw materials. SOS content has reached 5.17%. The POS content is lower than in CBS which is produced by variation of oil composition in raw material. POP symmetric triacylglycerols are decreased to 32.26% (Table 8.).

Table 8. Triglycerides Composition on CBS Poduced at 8 Hours Reaction Time

No	TAGs	Test Results (%)		
		Stearin Oil	Pumpkin Seed Oil	8 Hours Reaction Time
1	PPP	4,66	-	3,45
2	POP	54,05	-	32,26
3	PLP	-	-	0,6
4	POS	7,65	-	5,24
5	POO	25,1	10,04	26,01
6	SOS	1,53	9,24	5,17
7	SOO	5,49	10,39	10,18
8	OOO	-	15,98	5,8
9	PLO	2,3	25,44	10,46
10	OLO	-	19,95	1,15

CONCLUSION

Being mixed with pumpkin seed oil and interesterified with a sodium methoxide catalyst, the melting point of RBDPS is decreased from the previous 59^0C to 37,16^{o}C through eight hours interesterification process with 2 % of sodium methoxide to produce CBS. The FT-IR analysis of pumpkin seed oil shows a 3007 wave numbers which indicates C-H SP2 (C = C) of long chains. This is also supported by an absorption peak in 907 which indicates the presence of unsaturated fatty acid in oil. The FT-IR analysis of stearin oil shows weak wave of 3000s wave numbers refers to C-H SP2 for unsaturated bonds of aliphatic ester chains. However, The FT-IR of interesterification's product, CBS, shows the peak appearance in

3006. It indicates the unsaturated fatty acid chains which have been substituted to gliserol. The symmetrical triacylglycerols composition of interesterification's product, CBS, which is produced in 8 hours catalysed process consists of palmitic-oleic-palmitic (POP) 32,26 %, palmitic-oleic-stearic (POS) 5,24 %, and stearic-oleic-stearic (SOS) 5,17 %. There is an increase of SOS content and decrease of POP content on CBS when it is compared to RBDPS.

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