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CRYSTAL FORMING RATE AND DISTRIBUTION CHANGES OF MCT CONTENT IN PALM KERNEL OIL FRACTIONATION PRODUCT

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Abstract:

Palm kernel oil is considered a special oil since it contains medium chain tryglicerides (MCT), especially lauric acid that is easily digested and has a special character as cocoa butter substitutes (CBS). Palm kernel oil fractionation will produce a solid fraction (stearin) and a liquid fraction (olein) with specific characteristics (specialty fat) that the physico-chemical properties are highly dependent on the cooling treatment applied. In this research, 3 kinds of crystallization temperatures (18.0 oC, 19.0 oC, dan 20.0 oC) in various cooling rates and duration of the crystallization process, were examined for its effect on the crystal-forming rate of palm kernel oil and distribution changes of MCT content of fraction resulted. All tracks recorded during the cooling process had to be calculated to predict the crystal-forming rate in the crystallization process. In all cooling treatments, the amount of olein fraction produced decreased and the stearin fraction increased which was equal to the duration of the crystallization process. The setting of crystallization temperature at 18.0 oC produced a stearin forming rate higher than at temperatures of 19.0 and 20.0 oC. Forming rate of stearin (crystal) was contrary to the crystallization temperature and duration of the cooling period but not being affected by initial cooling temperature, initial cooling rate, duration of the cooling process to reach crystallization temperature, and average rate of oil cooling. Percentage of oil crystal-forming at 3 crystallization temperature equals to logarithmic of crystallization duration. The lower the crystallization temperature, the higher the rate of oil crystallization forming. As the increase of stearin produced during crystallization, MCT content was decreasing, but for olein, as the decreasing it during the crystallization period, the distribution of MCT content tends to increase.

Keywords: crystallization, lauric acid, PKO, specialty fat

1. Introduction

Consuming MCT can stimulate tyroid function and help reducing body weight. Palm kernel oil is also needed for oleochemical products as the main source of fatty acids such as caproat, caprilat, caprat, and commercial laurates. Palm kernel oil is also well known as laurat oil characterized by fast melted in body temperature and no greasy taste on tongue surface, make it potential to use as raw material for cocoa butter substitutes (Scrimgeour 2005, Wainwrigt 1999, Shukla 2006, Fuji Oil Europe 2004, PT Cahaya Kalbar Tbk 2004).

As well as oil and other natural vegetable oil, palm kernel oil has limited application in its original form because the specific chemical compositions. Vegetable oil is usually modified to vary its applications. Fat/oil modification usually is purposed to produce specialty fats which have higher added and economical value. The common modification methods such as hydrogenation, inter-esterification, blending and fractionation are used to reach the fat-based product target. During the modification, the initial physical and chemical properties can be changed (Chen *et al.* 2007, Shamsudin 2006).

Among all modification methods, the common method applied is fractionation (Ramli et al. 2008). Fractionation is the physical method using chrystallization properties from TAG to separate mixture into liquid fraction with low melting point and solid fraction with high melting point (Sarmidi et al. 2009). The concept of frcationation is based on the difference of TAG melting point (Huey et al. 2009). The successful of fractionation depends on the behaviour of TAG phase composition. The phase concept and behaviour do not depend only on TAG melting point or polimorphic characters, but also on involved TAG mixture that different in solid and liquid states (Calliauw et al. 2007).

By simple drying fractionation process under controlled condition, oil can be separated as liquid fraction (olein) and solid fraction (stearin) (Zaliha *et al.* 2004, Timms 1997, Timms 2005) which have their own physicochemical characteristics and specific applications (Sarmidi *et al.* 2009). Stearin from palm kernel oil generally used as raw material for oleic-chemical industries and cocoa butter substitutes. Meanwhile, olein is generally used as salad oil, cooking oil with high oxidative stability and oil as source of *medium chain triglycerides* (MCT) (Ong *et al.* 1995, Illingworth 2002, Scrimgeour 2005).

Oil fractionation by drying process generally divided into two stages, chrystallization to produce solid chrystall in a liquid matrices and filtration to separate the formed chrystal from liquid matrices. According to Timms (1997), the changes occured in molecular level during fat crystallization are the forming of nucleous (nucleation), the growth of nucleous and the changes of behaviour phase (*folymorphism*, *solid solutions*). The overall changes in this molecular level are greatly affected by treatment in physical level as removal of heat. Therefore, cooling method (cool temperature, decreasing temperature rate and the duration of cooling process applied) will determine the characteristics of fractionation yield produced.

Study on fat fractionation behaviour is very essential to conduct. Proper knowledge about fat fractionation kinetics is needed to regulate industry operational activity to produce end product in accordance with the purposed characteristics. Recently, the effect of temperature, cooling rate, and process length factors to behaviour of oil fractionation (especially laurat oil) and characteristics of fraction produced are not surely known. Hence, in phenomena occured due to the difference of factors applied can not be explained clearly and only small amount data for quantitatively kinetics are available. (Timms 2005, Chaleepa *et al*. 2010). Nevertheless, data availability related to behaviour of palm kernel oil fractionation is very needed for the development of fat based-end product regarding production intensification and extensification.

2. Material and method

Materials. Materials used in this research were *refined, bleached, deodorized palm kernel oil* (RBDPKO) (PT. BARCO, Jakarta). TAG standard was already known its TAG composition , RBDPO (PLO, PLP, OOO, POO, PPP) dan RBDPKO (CpCaLa, CaCaLa, CaLaLa, LaLaLa, LaLaO, LaLaM, LaMP, LaMM, LaMO, MPO, PLO/PPL, MOO).

Fractionation. Dry fractionation applied in this research was the modification methods conducted by Chaleepa *et al*. (2010) and Mursalin *et al*. (2013). To erase the memory (rejuvenating) and homogenization, palm kernel oil that would be fractioned heated at 70 ^{o}C for 10 minutes. Then, the liquid oil was placed in *crystallizer* and being cooled slowly with variation of cooling rate (0.1 – 0.9 ^{o}C/minute) until it reached the crystallization temperature wanted (18.0; 19.0 dan 20.0 ^{o}C) and left it in this temperature in a range of time((0 - 10 jam). During this crystallization process it was stirred with the rate of 7.5 rpm. After that, semi solid and wet mass from the oil crystallized was separated into fraction of stearin and olein using vacuum filter.

Fractionation yield. Rendemen calculation (yield) from palm kernel oil fractionation produced was done by sampling. 125 – 250 ml of frozen oil was taken from crystallisator tank and then filtered using vacuum with Whatman 40. After that, each fraction was scaled and recorded the volume.

Triasilgliserol Composition. Analyses of TAG composition refered to the method modified from *AOCS Official Methods* Ce 5c, 1997. TAG composition was analyzed using HPLC *Hewlett Packard series* 1100 with Refractive index, RI. Flow rate of mobile phase (aceton : acetonitril, 85 : 15 v/v) was 0.8 mL/min. The two columns used were C-18 (Microsorb MV dan Zorbax Eclipse XDB–C18, 4.6 x 250 mm, 5 µm) which was serial installed. Samples were dissolved into aceton with 5 % concentrate, and then 20 µL injected into HPLC. TAG composition analysis was applied to palm kernel oil before and after fractionation.

Statistical analysis. Mathematical relationship between cooling rate, crystallization temperature and duration of crystallization temperature with various of observed parameters was predicted with single or double linear regression. R^2 was used to measure variabilty proportion of independent variables for model used.

3. Result and Discussion

The forming of Stearin Fraction. In each cooling treatment, the amount of olein produced would decrease and stearin fraction would increase as the increasing of the duration of crystallization proses applied. The increasing rate of stearin, and the decreasing of olein during crystallization process was highly effected by cooling factors applied. The arrangement of oil crystalization temperature (eventhough in reality, the measured temperature was sllghty different with the defined temperature), initial average rate of cooling, the duration of cooling time to reach crystallization temperature, and average rate of oil cooling play important role in the rate of crystal formed (stearin fraction) during crystallization process. Record track for all oil cooling teratment produced and the rate of stearin formed was presented in Figure 1.

According to Mursalin *et al*. (2013), fractionation of lauric oil (including PKO) requires 3 cooling stages, the first stage is cooling which takes place at the beginning of cooling until it reaches the melting point temperature of the oil. The second stage is cooling from the melting point temperature of the oil to the set crystallization temperature. The third stage is cooling to maintain a constant oil temperature at the desired crystallization temperature. The cooling of the first stage may be carried out as quickly as possible but in the second stage, because it is the propagation phase of crystal nucleation, it must be carried out at a cooling rate of less than 0.176 °C/min. The cooling profile of PKO during fractionation can be seen in Figure 1.

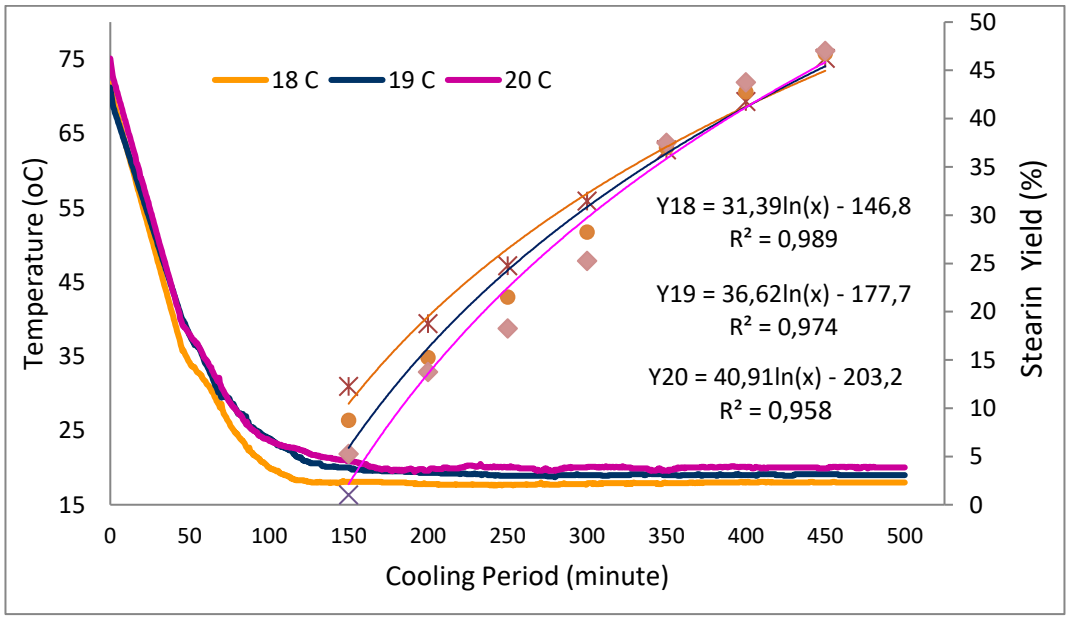

Figure 1. Track record of cooling treatment and stearin yield at 3 crystalization temperature

Based on Figure 1, percentage of oil crystal formed in each crystallization temperature during certain crystallization period was increasing following logaritmic equation. Individually, the equations was resulted as expression of each variation of cooling treatment applied. It indicates that every “track” of oil

temperature recorded during cooling process should be take into account to predict the rate of stearin formed during crystallization process. Mathematical equation resulted explain that percentage of oil crystal formed at 3 crystallization temperatures in line with the crystallization duration logaritmic. The lower crystallization temperature, the higher rate of oil crystal formed.

Figure 1 illustrates the relationship between the rate of stearin formed and duration of crystallization process at the crystallization temperature of 18.0 ^{o}C with the equation y = 31.39(Ln.x) - 146.8; at the crystallization temperature of 19.0 ^{o}C with the equation y = 36.62(Ln.x) – 177.7; at the and at the crystallization temperature of 20.0 ^{o}C with the equation y = 40.91(Ln.x) – 203.2; where y is the rate of oil crystal formed (%stearin/log crystallization time) and x is the crystallization process duration.

Palm kernel oil crystallization properties is diffrent from other oils, the state changing from solid into liquid occurs relatively in a narrow range of temperature. Solid state of palm kernel oil at room temperature (70°F/21.1°C), but will quickly and perfectly melt below body temperature (Gervajio 2005; O'Brien 2004). Palm kernel oil crystallization at temperature of 18.0 ^{o}C eventually results crystallization rate faster than conducted at higher temperature (20.0 ^{o}C).

The duration of oil cooling period to reach crystallization temperature had litle effect on the rate of oil crystal formation. In the observation range of 100 – 200 minutes, the faster oil was placed at its crystallization point, the faster for oil to begin crystalization process. Therefore, the crystallization occurs earlier so that more crystals was formed. For crystallization temperature lower than 18.0 ^{o}C or higher than 20.0 ^{o}C, it needs further verification.

MCT content of fractionation product. The solid and liquid form of palm kernel oil is largely determined by the accumulation of the molecular weight and melting point properties of each of its constituent triglycerides. Different triglyceride compositions will produce different melting points of oil (Gervajio 2005; O'Brien 2004). One of the main groups of triglycerides with high economic value found in palm kernel oil is medium chain triglycerides (MCT), namely triglycerides with 8-12 carbon chains.

The setting of oil crystallization temperature, initial cooling temperature, initial cooling rate, duration of cooling process to reach crystallization temperature, and average rate of oil cooling had not affect on the changing pattern of MCT content for each olein-stearin fraction. Description for the effect of the factors could see at Table 1 for stearin fraction and Table 2 for olein fraction. In all cooling treatments, the MCT content of the palm kernel oil stearin fraction produced would decrease while the MCT content of the olein fraction would increase in proportion to the longer of the crystallization process was applied. Each increase in crystallization period for 1 minute increased the MCT content of the PKO olein fraction by 0.015% and decreased the MCT content of the stearin fraction by 0.010% (**Figure 2**).

Tabel 1. The effect of various cooling factors on the MCT content of stearin fraction palm kernel oil during crystallization

Crys. Temp. (^{o}C)	Initial Temp. (^{o}C)	Time to reach Crys. Temp. (minutes)	Crystallization Period (minute)	Initial Cooling Rate (^{o}C/min)	Average Cooling Rate (^{o}C/min)	average of MCT (%)
	72,70	126,5	195	0,78	0,26	56,70
	71,20	129,1	194	0,77	0,30	56,54
18.0	75,10	183,75	250	0,66	0,30	56,92
	71,30	247,23	342	0,56	0,26	58,69
	72,50	235,82	258	0,57	0,21	57,22
19.0	74,90	278,08	354	0,39	0,41	58,06

	73,00	254,02	251	0,46	0,37	57,18
	79,30	204,75	379	0,6	0,44	58,52
	77,40	136,77	205	0,76	0,34	56,75
	72,20	162,57	305	0,73	0,29	57,44
	73,20	172,65	172	0,71	0,22	56,10
	77,20	114,92	275	0,99	0,47	57,37
	74,10	296,23	417	0,32	0,19	58,49
20.0	72,70	167,7	190	0,72	0,24	56,47
	72,60	130,27	243	0,77	0,20	56,82
	73,80	167,27	380	0,73	0,30	58,52

Tabel 2. The effect of various cooling factors on the MCT content of olein fraction palm kernel oil during crystallization

Crys. Temp. (°C)	Initial Temp. (°C)	Time to reach Crys. Temp. (minutes)	Crystallization Period (minute)	Initial Cooling Rate (°C/min)	Average Cooling Rate (°C/min)	average of MCT (%)
18.0	72,70	126,5	195	0,78	0,26	57,19
	71,20	129,1	194	0,77	0,30	56,51
	75,10	183,75	250	0,66	0,30	58,14
	71,30	247,23	342	0,56	0,26	59,21
	72,50	235,82	258	0,57	0,21	57,53
19.0	74,90	278,08	354	0,39	0,41	59,45
	73,00	254,02	251	0,46	0,37	58,32
	79,30	204,75	379	0,6	0,44	59,87
	77,40	136,77	205	0,76	0,34	57,63
	72,20	162,57	305	0,73	0,29	58,71
	73,20	172,65	172	0,71	0,22	56,32
20.0	77,20	114,92	275	0,99	0,47	58,03
	74,10	296,23	417	0,32	0,19	60,15
	72,70	167,7	190	0,72	0,24	57,19
	72,60	130,27	243	0,77	0,20	58,01
	73,80	167,27	380	0,73	0,30	60,12

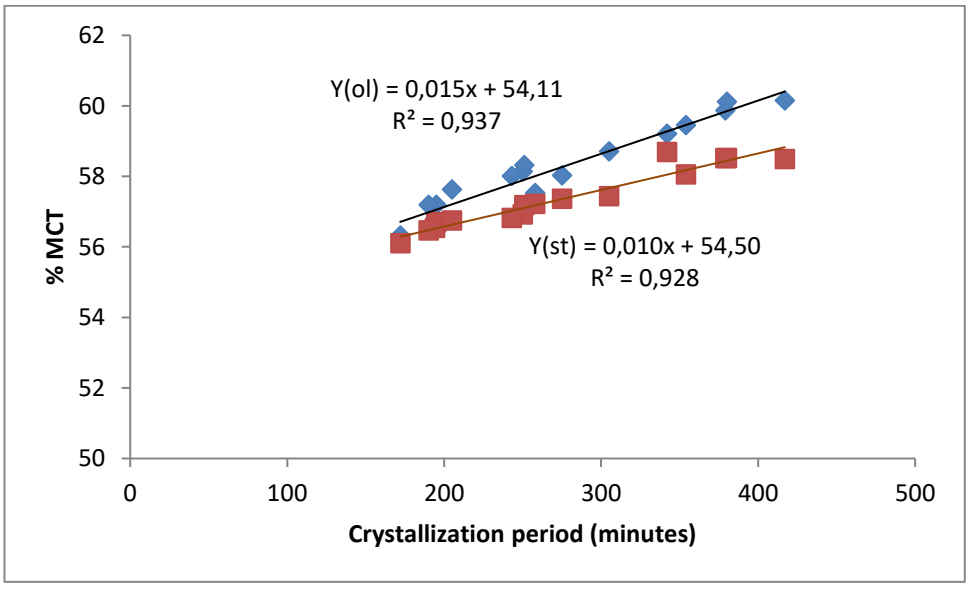

Figure 2. The correlation of crystallization period and %MCT of olein and stearin fractions of PKO

Conclusion

Every "track" recorded during cooling process must be taken into account to predict stearin forming rate in crystallization process. In all cooling treatment, the amount of olein fraction produced decreased and stearin fraction increased which equal to the duration of crystallization process. The setting of crystallization temperature at 18.0 ^{o}C produced stearin forming rate higher than at temperature of 19.0 and 20.0 ^{o}C. Forming rate of stearin (crystal) was contrary to the crystallization temperature and duration of cooling period but not being affected by initial cooling temperature, initial cooling rate, duration of cooling process to reach crystallization temperature, and average rate of oil cooling. Percentage of oil crystal forming at 3 crystallization temperature equals to logaritmic of crystallization period. The lower crystallization temperature, the higher the rate of oil crystallization forming. As the increasing of stearin produced during crystallization, MCT content was decreasing, but for olein, as the decreasing of it during crystallization period, the distribution of MCT content tends to increase.

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