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Crystallization kinetics of coconut oil based on Avrami model

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Abstract

It has been shown experimentally by many researchers that cooling rate and crystallization temperature affect the rate of crystal formation. In this study, crystallization kinetics of coconut oil was measured by monitoring the solid fraction of the oil using pulsed Nuclear Magnetic Resonance (pNMR). Four levels of cooling rate and crytallization temperature were studied. Parameters of crystallization kinetics are quantified by applying Avrami model. Avrami model was used to explain the mechanism of nucleation (Avrami index), crystallization rate constant and crystallization half-time. Crystallization was done by heating the oil at a temperature of 70°C for 10 minutes prior to rapid cooling to 29°C. Then, rate of cooling from 29°C to the crystallization temperature (critical cooling rate) was set below 2°C/minutes. During the process, the oil was stirred at 15 rpm. Solid fraction was measured periodically since the crystallization temperature was reached until maximum solid fraction was achieved. The results showed that Avrami model is able to quantitatively describe coconut oil crystallization kinetics. Lower critical cooling rate decreases Avrami index, crystallization half time but increases crystallization rate constant. Crystallization temperature has positive correlation with the crystallization rate contstant and Avrami index.

Introduction

Coconut oil is one of the most important oil crop in tropical regions. Therefore, an understanding of the fractionation characteristic of the edible oil is important for many practical applications in the oil and fat industry. Dry fractionation can be accomplished by crystallizing melted coconut oil and separating the crystals from the liquid oil by various means. The easiness of separating oil crystal from the liquid phase depends on the condition of crystallization process. Crystallization kinetics of fats, especially coconut oil, have not been well clarified so far and only few quantitative kinetic data are available which are based on empirical observations (Foubert *et al.*, 2003). Concrete information in the kinetic study of coconut oil crystallization has rarely been published.

Crystallization kinetics is typical to each of oil and a function of the characteristics of the oil and cooling treatment applied. Crystallization kinetics parameters that essential in oil namely the mechanism of nucleation, crystal growth rate and the maximum crystal produced. Nucleation can be referred to the initial of crystals formation. According to Garside (1987), nucleation only occurs if supercooling is applied, supercooling is a thermodynamic driving force for nucleation initiation. Furhermore, once the nuclei are formed, they grow and develop into crystals. Nucleation and crystal growth always occur simultaneously (Boistelle, 1988). Nucleation has the strongest predetermining influence on product properties, such as diversity of triacilglycerols (TAGs) in the crystalline product, maximum solid fat content produced, crystal habit or crystal size and size distribution (Ulrich and Strege, 2002; Liang *et al.*, 2003). All crystallization kinetic parameters cannot be determined directly from the experiment, but can be extracted from the quantities generated by plotting the experimental data to the model of crystallization kinetics equation.

Crystallization kinetics parameter was extracted by comparing mathematical model to experimental data. So far, the experimental data widely used for fitting the model is the enthalpy of crystallization kinetics measured by Differential Scanning Calorimetry (DSC) (Kellens *et al.*, 1990; Toro-Vazquez *et al.*, 2000; Vanhoutte *et al.*, 2002) and Solid Fat Content (SFC) measured with nuclear magnetic resonance spectroscopy (NMR) (Ng and Oh, 1994; Kloek *et al.*, 2000; Wright *et al.*, 2000). Models

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commonly used to describe kinetic of crystallization is Avrami model. Toro-Vazquez *et al.* (2002) used Avrami model to study the effect of differences in the mixture composition of stearin fraction of both palm oil and sesame seed oil. Campbell *et al.* (2004) used Avrami model for raw materials such as lard oil (fat form of blubber) and a mixture of palm oil stearin with canola oil on 2 kinds of emulsion homogenization pressure. Toro-Vazquez *et al*. (2002) applied Avrami model also for polar fat-free chocolate and natural cocoa at various crystallization temperatures.

According to MacNaughtan *et al.* (2006), Avrami model (equation 1) is frequently used to assess fat crystallization kinetics at isothermal condition describing the crystallization rate and the formation mechanism of fat crystal nuclei (nucleation).

$$1 - F = e^{(-zt^n)} \quad \text{......................... (1)}$$

F is the fraction of crystals formed during crystallization time t (min), z is the constant crystallization rate primarily determined by the crystallization temperature, and n is the Avrami index. Avrami model widely used primarily to determine n of which the value associated with the mechanism of crystal growth. According to Toro-Vazquez *et al*. (2002), in formation of homogeneous crystal nucleation, the crystallization process with n = 4 indicates that the mechanism of crystal growth is three-dimensional (3-D), n = 3 is a two-dimensional (2-D) and n = 2 is the one-dimensional (1-D). Non integer n values showed heterogeneously secondary crystal nucleation; z value in the Avrami equation is the combined rate constants involving the rate of nucleation and crystal growth, and F denotes reducedcrystallinity properties associated with the crystalline nature of the system at a given time (t) with the totalcrystallineachieved under the experimental conditions. The F value is calculated with a property proportional to the change in solid phase or crystallinity developed in the system as a function of time (Marangoni *et al.* 1999).

According to Campbell *et al.* (2004), higher values of n indicate greater dimensionality nucleus growth (progressing from rodlike to disklike to spherulitic) or a change in mechanism nucleation from instantaneous to progressive or sporadic nucleation. Avrami index, n, of the bulk fat is stongly dependent on temperature, with a significant increase as a function of temperature.

Toro *et al.* (2002) used the Avrami model to see fat crystallization kinetics in cocoa butter, milk fat, and milk fat fraction. Avrami index for cocoa butter, milk fat, and milk fat fraction are 4, 3, and 2 respectively. The aforementioned value indicates that each of oil, each nucleation occurs in heterogeneous nucleation, instantaneous nuclei, and high nucleation rate with each of crystal growth mechanisms each formed of polyhedral, plate-like, and cylinder.

In this study, based on changes in the amount of solid fraction (SFC) of oil, the effect of critical cooling rate and crystallization temperature of coconut oil is presented.Therefore, coconut oil cooled in three stages of cooling which are the initial cooling (temperature of 70-29°C), the critical cooling (from 29°C to the specified crystallization temperature), and cooling to maintain a constant oil temperature at the specified crystallization temperature (Mursalin *et al*. 2013).

This study is aimed to determine the effect of the critical cooling rate and crystallization temperature on the crystallization kinetics of coconut oil. The Avrami equation is used to extract kinetic parameters associated with the nucleation mechanism, crystal growth, and crystallization half-time.

Materials and Methods

The main materials used in this study are refined bleached deodorized coconut oil (RBDCNO) obtained from PT BARCO, Jakarta. Analysis result using gas chromatography (GC) and high performance liquid chromatography (HPLC), the coconut oil contains approximately 90% saturated fatty acids and half of them are lauric acid (51.73%). Coconut oil consists of 12 TAGs whereas the main TAG is trilaurin (LaLaLa) (20.43%).

Crystallization method applied to the sample has been modified from Zaliha *et al*. (2004) and Chaleepa *et al.* (2010). Prior to cooling, oil was heated at 70°C for 10 minutes to remove crystals that may still exist and erasing memory previously heated or cooled (rejuvenation). After that, from 70-29°C, the oil has been rapid cooled. Then a rate of cooling from 29°C to the crystallization temperature (critical cooling rate) was set below 2°C/minutes. During the process, the oil was stirred at 15rpm. After the crystallization temperature reached, the oil temperature kept constant until the end of the crystallization process. Schematic illustration of crystallization method is presented in Figure 1. To simplify the procedure, sampling was conducted by placing 3 ml of oil sample or about 2.5 cm height of tube of Bruker Minispec PC 100 NMR. These tubes were soaked its half part into oil (7.5 cm) and being cooled altogether. These tubes then being measured for the SFC content change as the representative of the overall of oil's SFC content change that had cooling treatment.

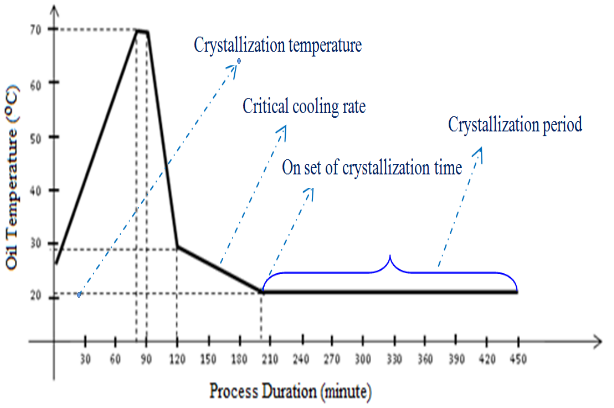

Figure 1. Scheme of crystallization method on coconut oil dry fractionation

Observation on solid fraction of oil during crystallization regularly was performed at the time of crystallization period (Figure 1). Crystallization period starts from the crystallization temperature was reached (on set of crystallization time) to a maximum solid fraction measured, indicated by solid fraction value that was relatively constant for the last 3 measurements. Heating and cooling oil are controlled using waterbath. Analysis of solid fraction in the oil is carried out using Bruker Minispec PC 100 NMR Analyzer.NMR is calibrated using standard solid fraction 0%, 31.5% and 72.9%.

Avrami model can be written as in linear form as follow (equation 2):

$$\ln[-\ln(1-F)] = \ln(z) + n[\ln(t)] \quad \text{.........................(2)}$$

Where F is the fraction of crystals formed during crystallization time t, z is the constant crystallization rate, and n is the Avrami index. Value of n and z respectively determined from the slope and intercept of the line. In this way, it is assumed that a single slope, which is associated as the n value, obtained from the plot of ln [-ln(1-F)] vs. ln (t).

According to MacNaughtan *et al.* (2006), z parameter associated with crystal growth rate but the unit depends on the n value. Therefore, $t_{1/2}$ is introduced to provide a better indicator for relative crystallization rate; $t_{1/2}$ is equivalent to required time to reach half of the maximum crystals amount that can be obtained (crystallization half-time), or written as:

$$t_{1/2} = \left(\frac{\ln 2}{z}\right)^{1/n} \quad \text{...................... (3)}$$

Results and Discussion

Avrami index

The experimental data is quantitatively compared to Avrami model to extract Avrami index, crystallization rate constant and half-time crystallization (Figure 2). Avrami index, n, is strongly affected by the critical cooling rate (vc, °C/min). Avrami index in the coconut oil crystallization has positive correlation with the critical cooling rate. The higher critical cooling rate result in bigger Avrami index (Figure 2a). Effect of crystallization temperature (T_{cr}, °C) on the Avrami index is less obvious than the effect of critical cooling rate (Figure 2b). Avrami index resulted from this study at various critical cooling rates were as follows: 3.377 ± 0.062 for vc<0.075 °C/min; 3.652 ± 0.058 to 0.075 <vc<0.125°C/min; 3.860 ± 0.048 to 0.125 <vc<0.175 °C/min, and 4.262 ± 0.083 for vc> 0.175 °C/min respectively.

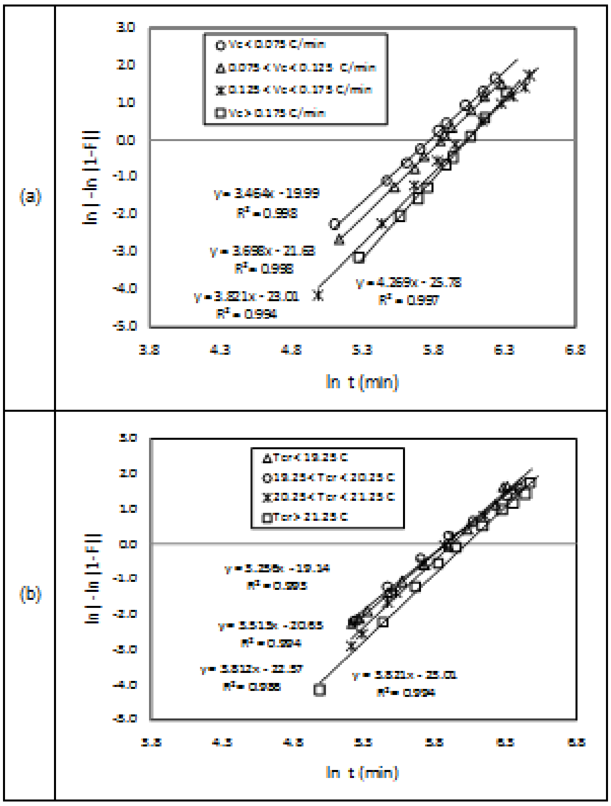

Figure 2.Plot of the experiments results with linear equation of Avrami model on four different critical cooling rate (a) and four different crystallization temperatures (b); v_c= critical cooling rate; T_{Cr} = temperature of crystallization; t = time of crystallization; F = solid fat fraction at certain crystallization period

The Avrami index ranges from 3 to 4 which means that crystal growth occurs in 2-3 dimension. The Avrami index value of 3 to 4 also indicates that crystallization involves the process of heterogeneous secondary crystal nucleation. It also means that the crystal growth occures in a progressive or sporadic manner, as reported by Toro-Vazquez *et al.* (2002) and Campbell *et al.* (2004).

Our previous study showed that stable coconut oil crystals was obtained at critical cooling rate smaller

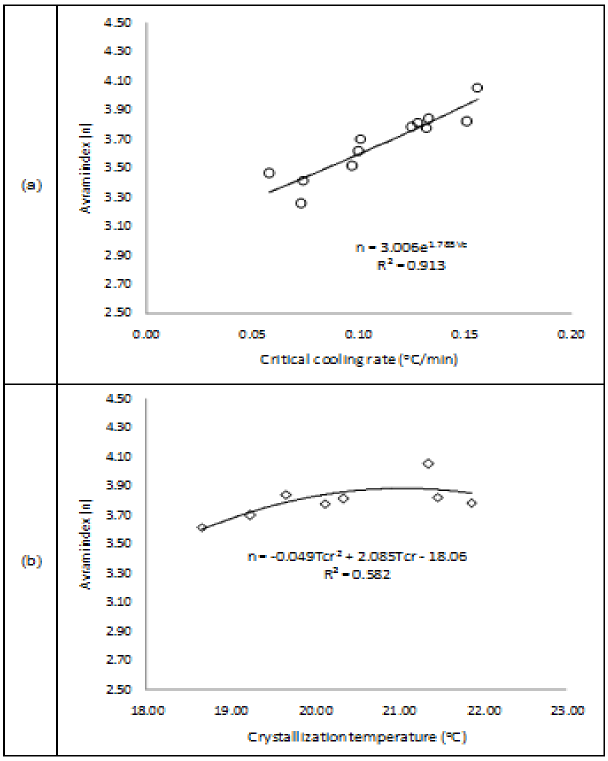

Figure 3. Relationship between Avrami index with critical cooling rate (a) and crystallization temperature (b); v_c = critical cooling rate; T_{Cr}= temperature of crystallization; n = Avrami index

than 0.176°C/min (Mursalin *et al.* 2013). Therefore, further analysis is conducted to study the relationship between the critical cooling rate (below 0.176°C/min) and crystallization temperature with Avrami index. The analysis showed that increase in the critical cooling rate exponentially increases the Avrami index (Figure 3a) and an increase in crystallization temperature increases the Avrami index polynomially (quadratic) as shown in Figure 3b. The relationship between the critical cooling rate with Avrami index can be described by the equation $n=3.006e^{1.785Vc}$. The relationship between the crystallization temperature with Avrami index can be explained by equation $n=-0.049Tcr^2+2.085\ Tcr\ -18.06$.

Crystallization rate constant and half-time crystallization

Comparison of experiment data and Avrami model also produces crystalline growth rate constant (z) which is directly related to $t_{1/2}$. Effect of critical cooling rate and crystallization temperature on z value, $t_{1/2}$ and Fmax can be seen in Figure 4. Figure 4 shows that the growth of coconut oil crystals during crystallization process exponentially decreases as function of critical cooling rate. The relationship between the critical cooling rate with the rate of crystal growth can be described by the equation $z = 576.3e^{-44.8Vc}$ (Figure 4a). The relationship between crystallization temperature with crystal growth rate

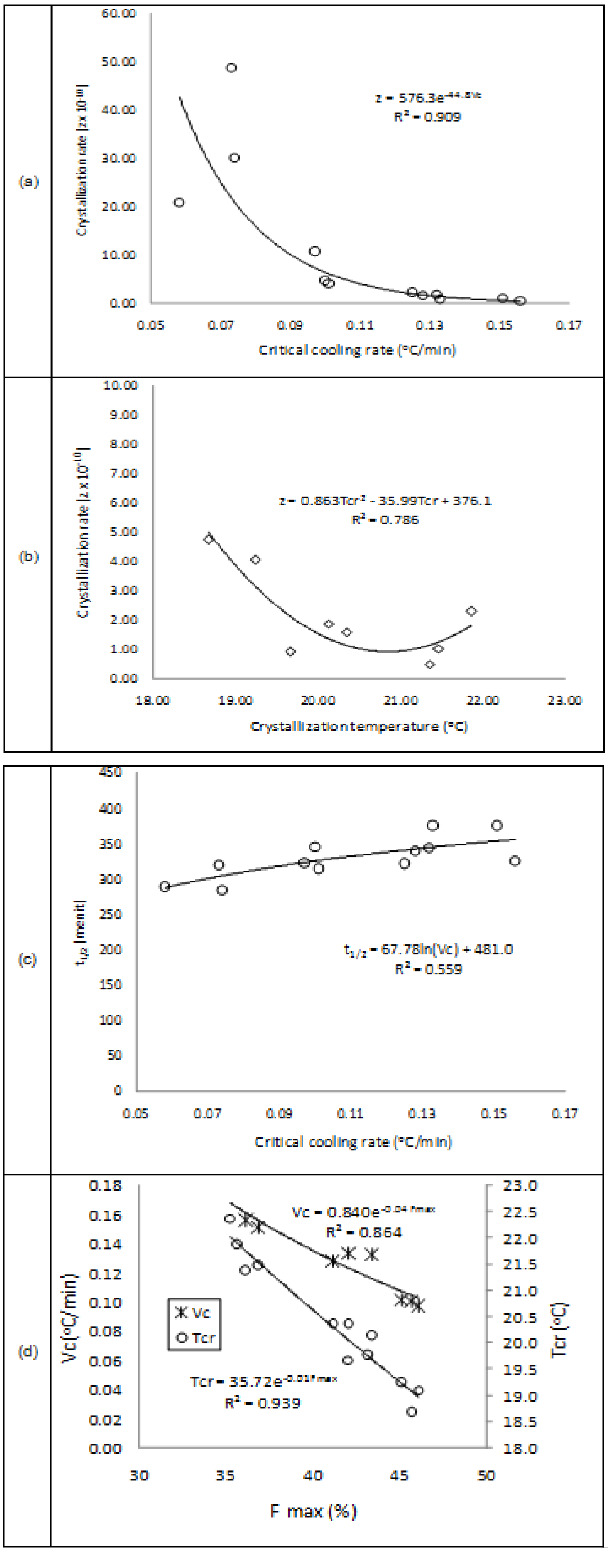

Figure 4. Relationship between crystal growth rate with critical cooling rate (a) and crystallization temperature (b), the relationship between critical cooling rate with a half-time crystallization (c), the relationship between critical cooling rate and crystallization temperature of the maximum solid fraction that can be achieved (d); v_c = critical cooling rate; T_{Cr} = crystallization temperature; Fmax = maximum solid fraction; z = crystal growth rate constant

can be described by the equation $z = 0.863Tcr^2 - 35.99Tcr + 376.1$ (Figure 4b).

The half-time crystallization of coconut oil logarithmically increases as function of cooling rate. The relationship between the crystallization half-time with a critical cooling rate can be described by $t_{1/2} = 67.78\ln(vc) + 481.0$ (Figure 4c). The oil amount that can be crystallized logarithmically decreases with critical cooling rate or crystallization temperature. The relationship between the maximum SFC with critical cooling rate can be described by $vc = 0.840e^{-0.04Fmax}$ whereas the crystallization temperature can be described as $Tcr = 35.72e^{-0.01Fmax}$ (Figure 4d).

Critical cooling rate significantly effect to Fmax of coconut oil. Lower cooling rate resulting in higher Fmax. This is consistent with research results of Arnaud *et al.* (2007) which revealed that lower cooling rate increases the maximum amount of crystals produced. This is becaused low cooling rate can provide longer supercooling conditions and provide opportunities for fat crystal to grow. This supercooling condition occurs due to the crystallization temperature applied is below the melting point of TAG. More fat crystals formed by the time of long supercooling conditions cause an increase in the rate of nucleation and greater crystal development.

After the fat nucleation step is completed, T_{Cr} determines Fmax that could be achieved. Higher T_{Cr} results in lower Fmax. This is related to process and mechanism of nucleus merging into the crystal (crystallization). Crystallization is demonstrated by changes in viscosity and oil phase from liquid to solid. Higher T_{Cr} causes the lower final SFC value due to decreased volume on crystalline phase when the temperature increases. The result is in line with Timms (2005); De-Graef *et al*. (2007);

Crystallization kinetics of coconut oil, in fact, has a little different from what happened in other vegetable oils such as palm oil and cocoa butter. Toro-Vazquez *et al.* (2002) reported that an increase in crystallization temperature tends to be followed by an increase in n and decrease in z, but an increase of oil cooling rate is not always followed by an increase in n or decrease in z because mixture composition of palm stearin and sesame oil had contribution in affecting the value of n and z samples. Toro-Vazquez *et al.* (2002) reported that cocoa butter crystallization occurs in two steps (first exotherm and second exotherm), the first step occured in a range of n value of 2.68-2.99 and z of 0.81-16.68 x 10^{-4} for four types of crystallization temperature (18.5-20.0^{o}C). In the second phase, the value of n increased to 3.47-4.23 and z decreased to 38.37-471.49 x 10^{-10}.

Conclusion

Avrami model is good to be used for describing the crystallization kinetics of coconut oil based on changes of oil solid fat content during the crystallization process. The model has the adjustability of more than 99% with the experimental results in this study.

A low critical cooling rate produces Avrami index and half-time crystallization were also lower but will produce high crystallization-rate-constant. Coconut oil crystallization temperature has positive correlation with the crystallization-rate-constant and the Avrami index but has negative correlation with the maximum SFC that can be achieved.

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