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TEKNOLOGI DAN
PENGENDALIAN PROSES
Changing on the Crystallization Kinetics of Chemically Interesterified Palm Olein Based on Foubert Model

Bangun P Nusantoro
Fakultas Teknologi Pertanian – UGM
Yogyakarta

Abstract

In this research, RBD-Palm Olein was chemically interesterified and the changing of its crystallization kinetics was determined based on the Foubert model. The initial RBD-Palm Olein had an Iodine Value of 57.82 and this value was not significantly altered during chemical interesterification (CI). From the HPLC measurement, it was found that the olein sample before CI consisted mainly of 2 types of triacylglycerols/TAG, namely POP (dipalmitoyl-oleoyl-glycerol) and POO (palmitoyl-dioleoyl-glycerol). Both contributed 28.10% and 24.76% of the total acylglycerols in the sample. The olein also contained a considerable amount of POL (10.98%), PLP (10.01%), POS (5.44%) and OOO (4.20%). After CI, there was an alteration of TAG composition as follows: POP (26.09%), POO (22.17%), POL (11.58%), PLP (7.32%), POS (4.98%) and OOO (5.97%). The changing of chemical compositions of the olein after CI influenced its crystallization kinetics. Before CI, the crystallization kinetics of the olein could be described by Foubert model as follows: $t_{ind_F}$ (0.468 h), $a_F$ (37.56 J/g), K (3.17 h$^{-1}$) and n (15.83). After CI, the crystallization kinetics of the olein have been altered to $t_{ind_F}$ (0.302 h), $a_F$ (41.63 J/g), K (2.46 h$^{-1}$) and n (12.43); where $t_{ind_F}$ (induction time), $a_F$ (maximum amount of crystallization), K (rate constant) and n (order of the reverse reaction).

Keywords: palm olein, interesterification, crystallization, kinetics and Foubert model.

Introduction

Palm oil is edible oil extracted from the pulp of the fruit of the oil palm (*Elaeis guineensis*). That palm tree is originated from tropical Africa and, for the first time, was brought to Southeast Asia in 1848 as an ornamental plant. For years, natural palm oil is admitted as an integral part of the diet in Africa and Southeast Asia (Spiller, 2004).

To improve the quality of palm oil as cooking oil, fractionation process is usually applied in order to get less saturated oil. Saturated oil is known to induce degenerative diseases (such as cardiovascular disease / CVD) by increasing total serum and LDL cholesterols. As the result, nowadays, consumers strongly demand healthier cooking oil in which the oil contains more unsaturated fatty acids (Strayer, 2006).

Fractionation of palm oil will produce palm stearin and palm olein where the later is the liquid fraction containing more unsaturated fatty acids. In order to get even higher quality of cooking oil, palm olein can be refractionated into palm super-olein and further refractionated into palm top-olein (Gibon, 2005). Unfortunately, palm olein has a distinctly slow crystallization kinetic during refractionation process.

To improve the physical properties of palm olein, some fat modification techniques may be used. One of those promising techniques is CI / chemical interesterification.

Chemical interesterification can alter the natural order of distribution of the fatty acids in triacylglycerols resulting products with different crystallization attributes compared to the initial oil. That process requires only heat and traces of alkaline catalysts. In addition, CI neither affects the degree of saturation nor causes isomerization of the fatty acid double bonds of the oil (O’Brien, 2009; Laning, 1985).

Fat crystallization will be important in the oil fractionation process where lipid products with various physical properties are manufactured by the crystallization technique (Hartel, 1992). To quantify the crystallization behavior of fats and oils, several mathematical models have been developed. The Avrami model has widely been used to describe the isothermal crystallization kinetics of fats. However, that model initially was developed for low molecular weight materials such as metals (Vanhoucke *et al.*, 2002; Kawamura, 1979).

Recently, Foubert *et al.*, (2003) formulated a fat model to represent the crystallization process as if it is a combination of a first-order forward reaction and a reverse reaction of order $n$. The equation is originally written in the form of a differential equation. For that,
the model has some advantages such as (1) easier to interpret the equation mechanistically; (2) easier to make minor changes to the equation on the basis of acquired knowledge; and (3) the model can be extended by incorporation of secondary models to describe non-isothermal crystallization kinetics. Because the good fits can be obtained by Foubert model, the model can act as a useful tool to describe crystallization process quantitatively.

In this research, the changing on crystallization kinetics of palm olein will be assessed after chemical interesterification process is carried out. The crystallization kinetic parameters will be determined based on Foubert model.

Materials and methods

Materials

The oil sample, Refined Bleached and Deodorized/ RBD palm olein, was purchased from a local refinery. In this experiment, all chemicals were of analytical or HPLC grade.

Chemical Interesterification Process

The process was run based on the procedure developed by Che Man et al. (1999) with a minor modification. RBD palm olein was dried in an oven at 110°C for 30 minutes and then added with anhydrous sodium sulfate in order to remove any residual moisture. An eight gram sample was filtered and flushed using nitrogen gas in a covered Erlenmeyer flask and then chemically transesterified using sodium methoxide (0.42%) as the catalyst. The Erlenmeyer flask was immersed in a water bath at 58°C for 389 minutes and constantly agitated during the process. At the end of the reaction, 2.0 g of citric acid and 100 ml of warmed distilled water were added to destroy the catalyst. Eventually, the sample was centrifuged (112 x g for 5 min.) and washed five times with a similar volume of warmed water before it was dried in the oven using the same procedure as described above.

Iodine Value / IV Measurement

The iodine value of the samples were determined using the AOCS officially recommended method Cd 1b-87. The olein sample was weighted to approx. 0.3500 g and then dissolved in cyclohexane. To react with the double bonds in the unsaturated oil, Wijs solution was chosen to be used.

Determination of Triacylglycerol Distribution

The distribution of the triacylglycerols / TAG was determined by HPLC, according to AOCS Official Method Ce 5b-89, with a differential refractometer as detector. Minor practical adjustments to the flow rate and mobile phase composition were made in order to improve TAG separation. The solvent was a mixture of 50% methanol and 50% chloroform (v/v) while the mobile phase was a mixture of 63.5% acetone and 36.5% acetonitrile (v/v). The flow rate was set at 1.2 ml/min for 50 minutes. The HPLC system consisted of Waters 515 HPLC pump, Waters 2414 refractive index detector, Waters 717 HPLC with auto sampler unit and Waters silica column.

Isothermal crystallization kinetic of palm olein

Differential Scanning Calorimetry / DSC analysis was the chosen technique to follow crystallization. The obtained data then were utilized to calculate the crystallization kinetics based on Foubert model. The relative amount of material crystallized as function of time was calculated by integration of the isothermal DSC curves.

Differential Scanning Calorimetry analysis was carried out using a Q1000 DSC (TA Instruments, New Castle, USA) with a refrigerated cooling system (TA Instruments) using aluminum SFI pans. Calibration was made with indium and n-dodecane standards. Nitrogen was used as purge gas in order to prevent condensation in the cells. An empty aluminum SFI pan was used as reference. The sample was heated at 65°C for 10 minutes to erase all crystal memory then fast cooled at a cooling rate of 8°C/min to the isothermal crystallization temperature of 5°C for 180 minutes.

After DSC analysis, Foubert model was fitted to the obtained data by non-linear regression using Sigmaplot 2000 software (SPSS Inc., USA). The model has four parameter estimations and the algebraic equation of the model is presented below (Foubert et al., 2002).

\[ f(t) = a_F \times \left[ 1 - \left( \frac{(1 - F)^{1-n-1}}{\frac{K}{t_{mid_F}} + 1} \right)^{n} \right] \]

Where \( f \) is the amount of crystallization at the time \( t \). The first parameter, \( a_F \), is the maximum amount of crystallization (expressed in J/g (latent heat) on DSC measurements). The second parameter, \( t_{mid_F} \), is defined as the time needed to obtain \( 5\% \) of crystallization. The other two kinetic parameters are \( K \) (rate constant) and \( n \) (order of the reverse reaction).

Results and Discussion

The Alteration of the Chemical Composition

Palm olein sample was obtained from a single stage dry fractionation of RBD palm oil. The triacylglycerol distribution of RBD palm olein before chemical interesterification was presented in Table 1. It was shown that the initial palm olein contained four major triacylglycerols, namely POP (28.10%), POO (24.76), POL (10.98%) and PLP (10.01%). With respect to the higher ratio of unsaturated triacylglycerols of palm olein compared to that of RBD palm oil, the olein will be visually present as clear liquid at room temperature contrasted to the palm oil which will exist as a mixture of liquid and solid.

After chemical interesterification, triacylglycerol distribution was slightly altered. The four main triacylglycerols in addition to triunsaturated and trisaturated encountered fairly clear concentration changes as shown in Table 1. There was a decrease in
The tendency of fatty acid distribution among triacylglycerols seemed to follow the law of probability. The triacylglycerol content of type S₃ (trisaturated) and U₃ (triousaturated) was generally higher than in the initial palm olein in which that palm olein contained very little triacylglycerols of those types (for example, from 1.13% to 2.68% of S₃ following chemical interesterification). Conversely, the triacylglycerol content of type S₂U (monounsaturated) and SU₂ (diunsaturated) was significantly lower than in the initial palm olein in which that palm olein abundantly contained triacylglycerols of those types (for example, from 44.57% to 39.10% of S₂U following chemical interesterification). According to Rousseau and Marangoni (2002), chemical interesterification will result in complete fatty acid randomization among all the triacylglycerols according to the laws of probability.

The iodine value of the initial palm olein was 57.82 and, after chemical interesterification, the iodine value remained approximately at similar value (iodine value of CI palm olein was 57.79). According to Silva et al. (2009), interesterification does not cause substantial modification of the fatty acids. As the fatty acids of palm olein are not changed and only randomly distributed, the degree of saturation should remain constant.

The changes on chemical composition of RBD palm olein after chemical interesterification are expected to deliver significant effects to its crystallization kinetics. The triacylglycerol profile is considered as the key for physical properties of the oil (Ribeiro et al., 2009). Different type of triacylglycerols will hold different physical and thermal properties. With respect to the thermal properties of the oil, trisaturated triacylglycerols will have higher melting points while triousaturated triacylglycerols will possess lower melting points. The rest will have melting points in between. For example, tripalmitin has a melting point of 66.2°C but triolein has a melting point only of 5.1°C (Ghotra et al., 2002). When the concentration of both trisaturated and triousaturated triacylglycerols increases, the melting range among triacylglycerol fractions in palm olein becomes wider. And then, interosolubility effect of similar triacylglycerols will also diminish. As result, the separation process during dry fractionation of palm olein can be run much easier.

The Alteration of the Crystallization Kinetics

Chemical interesterification is expected to function in alteration of the kinetic parameters of palm olein crystallization. Four kinetic parameters of palm olein crystallization as measured by Foubert model were presented in Table 2. The data were shown that all kinetic parameters had lower values following the chemical interesterification except for the maximum amount of crystallization / \(a_F\).

Table 1. Chemical Composition of RBD Palm Olein

<table>
<thead>
<tr>
<th>Triacylglycerol* (%)</th>
<th>RBD palm olein</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP</td>
<td>0.26</td>
<td>1.46</td>
</tr>
<tr>
<td>POP</td>
<td>28.10</td>
<td>26.09</td>
</tr>
<tr>
<td>POS</td>
<td>5.44</td>
<td>4.98</td>
</tr>
<tr>
<td>SOS</td>
<td>0.20</td>
<td>0.18</td>
</tr>
<tr>
<td>POO</td>
<td>24.76</td>
<td>22.17</td>
</tr>
<tr>
<td>SOO</td>
<td>2.82</td>
<td>1.73</td>
</tr>
<tr>
<td>PLP</td>
<td>10.01</td>
<td>7.32</td>
</tr>
<tr>
<td>MLP</td>
<td>0.82</td>
<td>0.53</td>
</tr>
<tr>
<td>POL</td>
<td>10.98</td>
<td>11.88</td>
</tr>
<tr>
<td>OOO</td>
<td>4.20</td>
<td>5.97</td>
</tr>
<tr>
<td>PLL</td>
<td>2.75</td>
<td>2.35</td>
</tr>
<tr>
<td>LOL</td>
<td>0.50</td>
<td>1.32</td>
</tr>
<tr>
<td>LOO</td>
<td>2.03</td>
<td>4.38</td>
</tr>
<tr>
<td>Trisaturated</td>
<td>1.13</td>
<td>2.68</td>
</tr>
<tr>
<td>Monounsaturated</td>
<td>44.57</td>
<td>39.10</td>
</tr>
<tr>
<td>Diunsaturated</td>
<td>41.31</td>
<td>38.13</td>
</tr>
<tr>
<td>Triunsaturated</td>
<td>6.73</td>
<td>11.67</td>
</tr>
</tbody>
</table>

| Iodine value | 57.82 | 57.79 |


Table 2. Crystallization Kinetics of RBD Palm Olein

<table>
<thead>
<tr>
<th>Kinetic parameters*</th>
<th>RBD palm olein</th>
</tr>
</thead>
<tbody>
<tr>
<td>(t_{indF}) (h)</td>
<td>0.468</td>
</tr>
<tr>
<td>(a_F) (J/g)</td>
<td>37.56</td>
</tr>
<tr>
<td>(K) (h⁻¹)</td>
<td>3.17</td>
</tr>
<tr>
<td>(n) (-)</td>
<td>15.85</td>
</tr>
</tbody>
</table>

* Based on Foubert model.

In the data calculation, we used the assumption that F equals to 1% of crystallization. Therefore, the parameter \(t_{indF}\) was defined as the time needed to obtain F (1%) of crystallization. As shown in Table 2, induction time \(t_{indF}\) of palm olein crystallization before CI was 0.468 h and, after CI, the value was decrease to 0.302 h. It meant that chemically interesterified palm olein would likely form crystal nuclei faster than the initial palm olein. According to Loisel et al. (1998), the high melting crystal will first be formed during cooling. They also suggested that the nucleation process may start from complex lipid and trisaturated triacylglycerols. This was in agreement with the fact that chemically interesterified palm olein...
had a higher trisaturated content (2.68%) than that of the initial palm olein (1.13%).

The parameter \( a_F \) indicates the maximum amount of crystallization which is measured as \( a_F \) (% solid fat) or \( a_F \) (J/g) depending on the measuring technique. As we used DSC to collect the data, the parameter \( a_F \) was given a dimension of J/g. Table 2 showed that there was an increase of \( a_F \) value from 37.56 J/g (initial palm olein) to 41.63 J/g (CI palm olein). Thus, at any similar crystallization condition, chemically interesterified palm olein will likely have more crystals compared to the initial palm olein. One of the reasons is that the lower equilibrium amount of solid fat can be caused by the higher concentration of diunsaturated oils. Generally, diunsaturated triacylglycerols have the double bond in the \( sn-3 \) position. The double bond may interrupt the molecular packing of the triacylglycerols (Chaiseri and Dimick, 1989).

The parameter \( K \) is the rate constant of the crystallization model (h\(^{-1}\)). The higher value of \( K \) indicates the shorter the time needed to reach any measurable amount of crystallization or the faster the time needed to complete the crystallization process. From Table 2, \( K \) of the initial palm olein had higher value (3.17 h\(^{-1}\)) compared to that of chemically interesterified palm olein (2.46 h\(^{-1}\)).

The content of monoaoylglycerols and diacylglycerols of edible oils may increase after chemical interesterification process (Laning, 1985).

The kinetic parameter \( n \) is related to the order of the reverse reaction (dimensionless). The existence of a reverse reaction can be demonstrated by remelting, redissolving, or the both combination. The value of \( n \) is also linked to the degree of curve asymmetry. According to Foubert (2003), the sigmoid curve is perfectly symmetric when the value of \( n \) is 2. If the value of \( n \) is larger than 2, the beginning of the crystallization process is faster than the end and vice versa. Table 2 showed that both the initial and CI palm oleins had the values of \( n \) higher than 2. Palm olein initially had an \( n \) value of 15.85 and this \( n \) value was altered to 12.43 following chemical interesterification.

**Conclusion**

Chemical interesterification slightly altered the triacylglycerol distribution of palm olein. Even so, slightly modification on the chemical composition of palm olein affected quite strongly on its crystallization kinetics. Chemically interesterified palm olein had shorter induction time and higher on maximum crystallinity but slower in the rate of crystallization process. The changes on crystallization kinetics could be exploited to design a better fractionation process.

**References**


