

Crystallization properties of palm oil by dry fractionation

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Abstract

The crystallization, thermal, physical, chemical and morphological properties of palm oil were investigated using differential scanning calorimetry, polarized microscopy, pulsed nuclear magnetic resonance (NMR) and gas chromatography (GC). The palm oil was fractionated into various stearin and olein (with iodine values (IV) > 63) fractions by means of a dry fractionation process. During the cooling sequence, samples were taken at regular intervals from the crystallizer and analyzed for their iodine values, chemical compositions and physical behaviour. The physical properties of olein and stearin fractions, such as cloud point, slip melting point and solid fat content, were dependent on the crystallization temperatures. The iodine values of the olein and stearin fractions increased as the crystallization temperature decreased and both fractions started to cloud at lower temperatures. The palmitic acid content of stearin and olein fractions was also affected by the crystallization temperatures.

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1. Introduction

Palm oil contains a mixture of high and low melting triglycerides. At ambient temperatures, higher melting triglycerides will crystallize into a solid fraction called stearin, while the lower melting triglycerides will remain in a liquid form called olein. By a simple dry fractionation process under various controlled conditions, palm oil can be resolved into a liquid and various grades of palm stearin.

The dry fractionation process is based on differences in melting points of the component triglycerides and partial glycerides (Ng, 1989; Siew & Ng, 1995; Siew & Ng, 1996) and is a thermomechanical separation process where the high and low melting triglycerides are separated by partial crystallization, followed by filtration (Kellens, 1993).

The crystallization process of fats can be divided into three basic steps: super cooling of the melt, formation of

crystal nuclei and crystal growth. The crystal shape and size distribution are determined by the way the melted oil is cooled and agitated (Taylor, 1976; Russell, 1986, Chap. 10).

In this work, palm oil was fractionated by a single stage fractionation process to obtain an olein fraction with IV > 63 and palm mid-fractions of various IV values at different crystallization temperatures. The physical and chemical properties of the olein and stearin fractions were then analyzed.

2. Materials and methods

2.1. Materials

Commercial refined, bleached and deodorized palm oil (RBD palm oil), of iodine value (IV) 52.0, was purchased from Lam Soon Oils and Fats, Petaling Jaya, Selangor, Malaysia and used as such without further treatment to simulate actual plant fractionation conditions. All other materials were of analytical grade.

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2.2. Fractional crystallization

The oil was melted and kept homogenized at 70 °C to destroy all crystal memory. The melted oil was charged into a 5 kg water-jacketed crystallizer, then agitated with stirring rate of 25 rpm, and cooled in a controlled manner by circulating chilled water to the crystallizer for 120 min for each crystallization temperature. The crystallization temperatures of 18, 15, 11 and 9 °C were investigated. The olein and stearin fractions were abbreviated as Ol and St, respectively. During the cooling process, supercooling of the oil occurred, resulting in nucleation and crystal growth.

After stabilization, the crystal and oil phases appeared as thick semi-solid slurries. The slurry was then separated into olein and stearin by a vacuum filtration. During the cooling sequence, samples were taken at regular intervals from the crystallizer for their chemical composition and physical behaviour analyses.

2.3. Analytical methods

2.3.1. Cloud point (CP)

Cloud point is a test to determine the temperature at which the oil begins to cloud, resulting from crystallization under controlled cooling. The AOCS official method Cc6-25 (AOCS, 1990) was used to ascertain the cloud point. Triplicate measurements were carried out for each sample.

2.3.2. Iodine value by Wiji's method (IV)

The iodine value was determined according to the AOCS official method Cd-25 (1990). The observation was based on the three measurements.

2.3.3. Fatty acid composition (FAC)

Fatty acid compositions were determined as fatty acid methyl esters (FAME) according to PORIM's test method (PORIM, 1995). Analysis was conducted using a SGE, PBX 70 fused silica capillary column (60 m × 0.25 mm i.d.) with a split ratio of 1:00 flow rate of 0.85 ml N₂/min, and oven temperature was set isothermally at 230 °C on a Hewlett–Packard 5890 gas chromatography.

2.3.4. Determination of solid fat content (% SFC)

The solid fat content of oil was measured using pulsed nuclear magnetic resonance (NMR) spectrometry (Bruker minispec P20:20 Mhz, Karlsruhe, Germany). The PORIM parallel test method was used. Solid fat content of the sample before (slurry), and after filtration (olein and stearin) fractions were measured at each separation temperature. The sample in the NMR tube was first melted at 70 °C for 30 min, followed by chilling at 0 °C for 90 min prior to measurement

(PORIM, 1995). Melting, chilling and holding of samples were carried out in pre-equilibrated thermostatted water bath. The values of % SFC were based on three measurements.

2.3.5. Thermal behaviour by differential scanning calorimetry

The thermal properties of the samples were measured using a differential scanning calorimeter Model DSC-7 (Perkin–Elmer, Norwalk, Connecticut, USA). The instrument was attached to a data processing unit (Perkin–Elmer Thermal Data Station). The instrument was calibrated by using indium for the higher temperature range and *n*-decane for sub-ambient temperatures. The sample was hermetically sealed in aluminium sample pan. The sample weight used was from 3 to 5 mg with an empty aluminium sample pan acting as the reference. The sample was heated up to 70 °C and held at this temperature for 10 min to ensure that the fat was totally melted and all the nuclei was destroyed. The sample was then cooled to –40 °C at a cooling rate of 5 °C/min. The cooling thermogram was recorded. The sample was then held at –40 °C for 10 min before being heated to 70 °C at a heating rate of 5 °C/min. The melting thermogram was also recorded.

2.3.6. Crystal morphology

Crystal morphology was observed using a polarised light microscope (Olympus) equipped with a temperature-controlled stage. The crystals, at each crystallization temperature, were photomicrographed at magnification of 200 times.

3. Results and discussion

3.1. Cloud point and iodine value

The cloud point is related to the unsaturation of the samples; the more unsaturated the samples, the lower will be the cloud point. Fig. 1(a) shows that, after RBD palm oil, with an iodine value of 52 and a cloud point of 21.4 °C, was fractionated at 9 °C, the IV of the olein obtained (Ol9 °C) was 63.1 with a cloud point of 1.6 °C and the oil was in liquid form at room temperature. The lower the crystallization temperatures, the higher the iodine value of the olein and stearin fractions, as shown in Figs. 1(a) and (b). Similarly, Figs. 2(a) and (b) shows that, lower the crystallization temperatures, the lower are the cloud points of the fractions.

A clear correlation between IV and CP of the fractions at different crystallization temperatures, is also shown in Figs. 3(a) and (b). The olein fractions with high IV had low cloud points, while the low IV fractions had high CP.

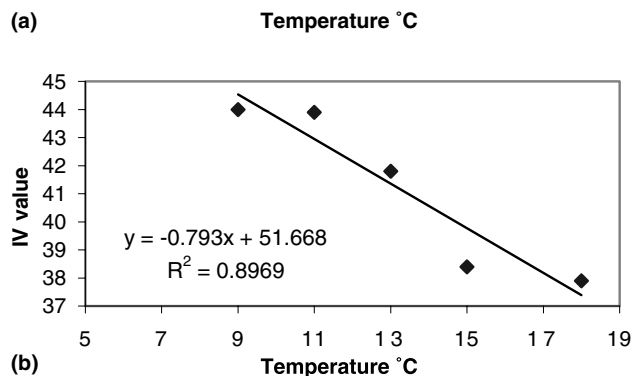
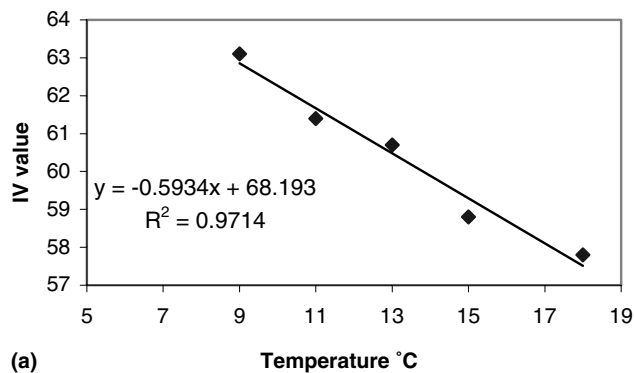


Fig. 1. (a) Iodine values (IV) of olein fractions at different crystallization temperatures. (b) Iodine values (IV) of stearin fractions at different crystallization temperatures.

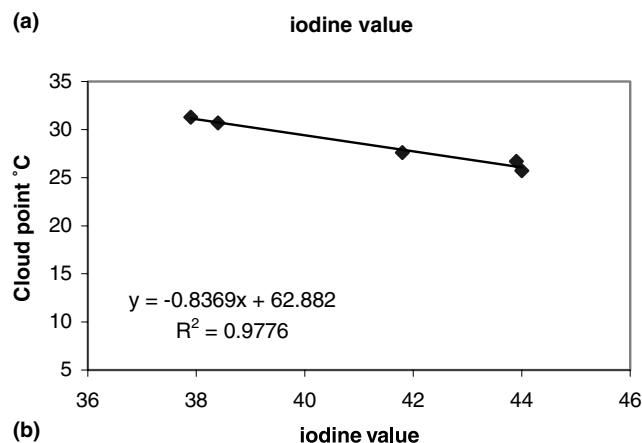
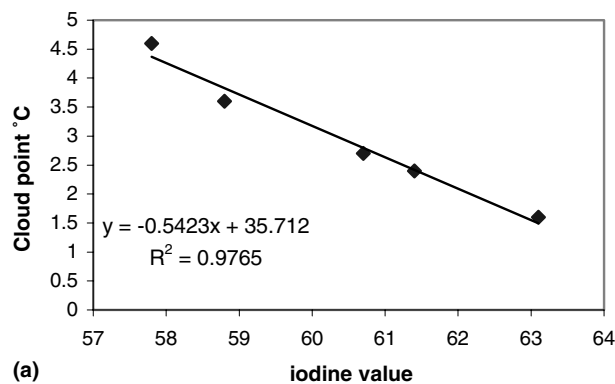


Fig. 3. (a) Iodine values (IV) and cloud points (CP) of olein fractions. (b) Iodine values (IV) and cloud points (CP) of stearin fractions.

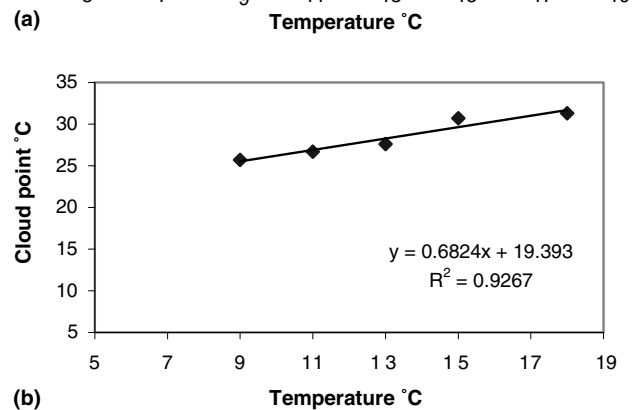
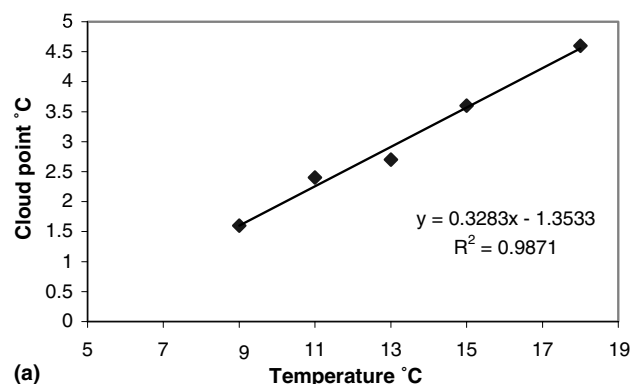


Fig. 2. (a) Cloud points (CP) of olein fractions at different crystallization temperatures. (b) Cloud points (CP) of stearin fractions at different crystallization temperatures.

3.2. Fatty acid composition

During either double or single-step fractionation, the chemical compositions of the liquid and solid phases triglycerides are gradually concentrated in the solid phase (stearin), leaving behind a more unsaturated liquid phase (olein). Table 1 shows the fatty acid compositions of the stearin and olein fractions. Originally, the RBD palm oil contains 44.2% of the saturated acid C16:0 and 40.4% of the unsaturated acid C18:1.

As the crystallization temperature is reduced to 9 °C, the olein fractions show a decrease of C16:0, from 44.2% to 34.4%, and an increase in C18:1, from 40.4% to 46.1%. The stearin fractions show a decrease of C16:0, from 51.0% to 48.9% and an increase of C18:0, from 30.8% to 36.0%. This shows that the olein fractions have become less saturated with reductions of C16:0 and C18:0 contents.

3.3. Solid fat content (% SFC)

The % SFC of each fraction was measured as a function of temperature. Fig. 4(a) show the solid fat content of RBD palm oil and stearin fractions obtained at various temperatures. The SFCs of stearin fractions are all higher than the SFC of RBD palm oil and are

Table 1
Fatty acid composition of RBD palm oil, and olein and stearin fractions at different crystallization temperatures

| Sample | Fatty acid composition (%) | | | | | | | | |
|-----------|----------------------------|------|------|------|------|------|------|------|------|
| | 12:0 | 14:0 | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 | 18:3 | 20:0 |
| RBDPO | 0.3 | 1.1 | 44.2 | 0.1 | 4.0 | 40.4 | 9.8 | 0.3 | – |
| St18 (°C) | 0.5 | 1.4 | 51.0 | 0.2 | 30.8 | 3.7 | 7.4 | 0.3 | 4.7 |
| St15 (°C) | 0.2 | 1.2 | 54.3 | 0.2 | 32.0 | 4.5 | 7.6 | 0.2 | 6.5 |
| St13 (°C) | 0.3 | 1.3 | 54.4 | 0.1 | 32.3 | 3.7 | 7.5 | 0.3 | – |
| St11 (°C) | 0.2 | 1.1 | 50.0 | 0.1 | 35.3 | 4.5 | 7.9 | 0.4 | 7.5 |
| St9 (°C) | 0.2 | 1.1 | 48.9 | 0.2 | 36.0 | 4.6 | 8.2 | 0.4 | 0.4 |
| O118 (°C) | 0.4 | 1.0 | 37.9 | 0.1 | 3.7 | 44.0 | 11.1 | 0.3 | 0.7 |
| O115 (°C) | 0.4 | 1.0 | 37.0 | 0.1 | 3.6 | 44.5 | 11.4 | 0.4 | 0.7 |
| O113 (°C) | 0.4 | 1.0 | 36.5 | 0.1 | 3.4 | 45.4 | 12.3 | 0.3 | 0.4 |
| O111 (°C) | 0.4 | 1.1 | 34.4 | 0.1 | 3.3 | 45.3 | 12.2 | 0.1 | 1.0 |
| O19 (°C) | 0.4 | 1.1 | 34.4 | 0.1 | 3.2 | 46.1 | 12.9 | 0.7 | 0.3 |

All the readings were based on means of three measurements (RBDPO, refined bleached and deodorized palm oil; St, stearin fraction; Ol, olein fraction).

melted at temperatures above 45 °C. This is due to the fact that the stearin fractions contain higher amounts of saturated fat with higher melting points and are crystallized out at higher temperatures during the fractionation process

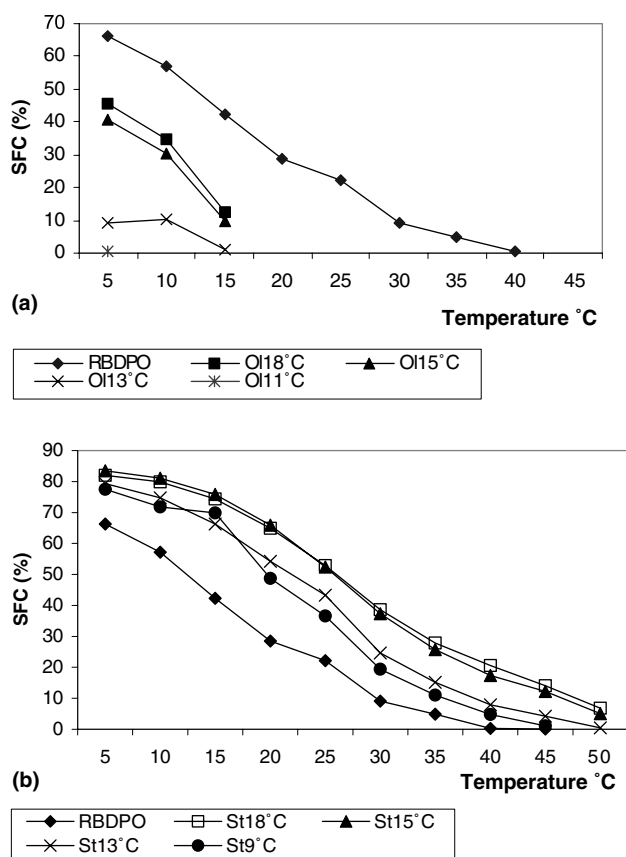


Fig. 4. (a) Solid fat content (% SFC) of RBD palm oil and olein fractions. (RBDPO, refined bleached and deodorized palm oil; Ol, olein fraction). (b) Solid fat content (% SFC) of RBD palm oil and stearin fractions. (RBDPO, refined, bleached and deodorized palm oil; St, stearin fraction).

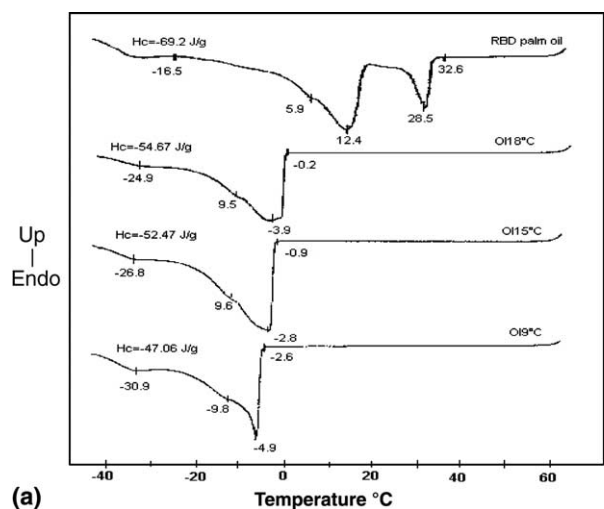
Figs. 4(a) and (b), show the solid fat contents of RBD palm oil, stearin and olein fractions at various temperatures. The olein fraction curves show lower solid fat contents at lower temperatures, and are completely melted below body temperature whereas, the solid fat of RBD palm oil still retains 22.2% solid fat. As the crystallization proceeds, the solid fat of the olein fraction (O19 °C) is reduced to 8.3% at 0 °C only.

3.4. Thermal behaviour by differential scanning calorimetry (DSC)

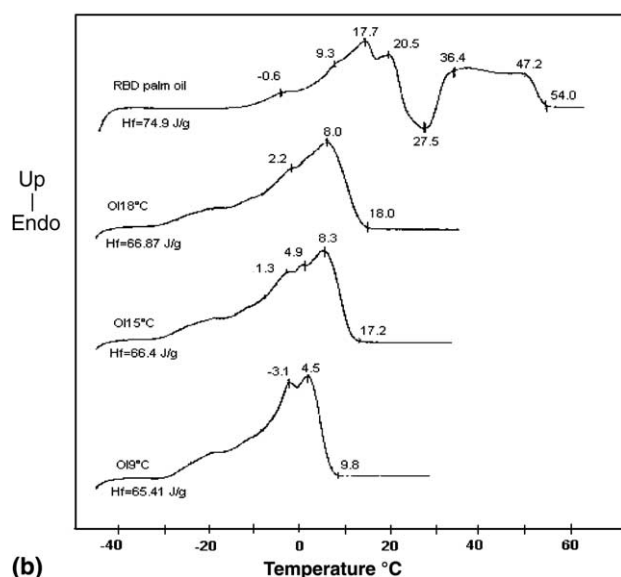
3.4.1. Cooling thermograms

The cooling thermograms of RBD palm oil, stearin and olein fractions are shown in Fig. 5. The thermogram of RBD palm oil shows two exothermic peaks. Exothermic peaks, at 28.5 °C, represent the high melting TAGs while the 12.4 °C, with shoulders, at 5.9 and –16.5 °C represents the lower melting TAGs. As the crystallization temperature was lowered down to 9 °C, the olein fraction showed a single crystallization peak at –4.9 °C with two small shoulders at –9.8 and –30.9 °C. At the same time, ΔH_c (heat of crystallization) of RBD palm olein is reduced to 47.06 J/g for the 9 °C olein fraction as compared to a value of 69.2 J/g for RBD palm oil.

Fig. 6 shows the cooling thermograms of soft and hard stearins. The harder stearin at 18 °C (St18 °C) started to crystallize at 29.9 °C with a sharp peak at 25.9 °C, followed by a broader peak with shoulders at 1.3 and –8.5 °C, respectively. The softer stearin at 9 °C (St9 °C) started to crystallize at a lower temperature of 19.2 °C with a sharp peak at 11.4 °C and a broader peak at –2.0 °C with a shoulder at –7.6 °C. The ΔH_c values for stearin fractions were observed to be higher than that of RBD palm oil. The results show that the stearin fractions have occluded a fair amount of olein within the crystal matrix during the fractionation process, as indi-



(a)



(b)

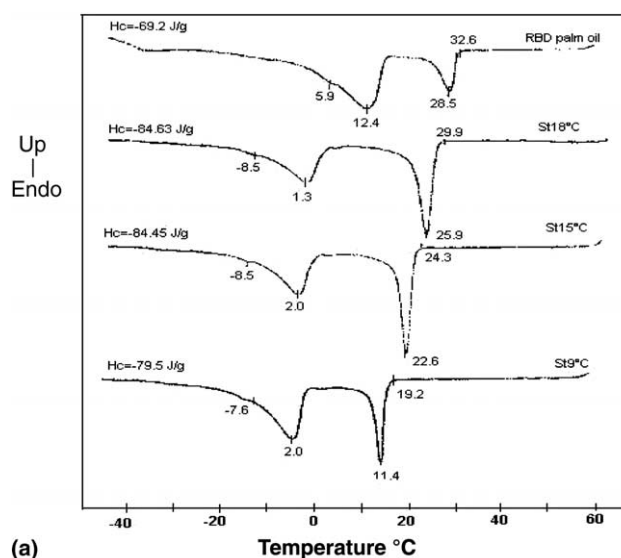
Fig. 5. (a) DSC cooling thermograms of RBD palm oil and olein fractions (abbreviations as indicated in Fig. 4(a)). (b) DSC melting thermograms of RBD palm oil and olein fractions (abbreviation as indicated in Fig. 4a).

cated by the two exothermic peaks shown in Fig. 6. The low and high temperature peaks represent olein and stearin, respectively.

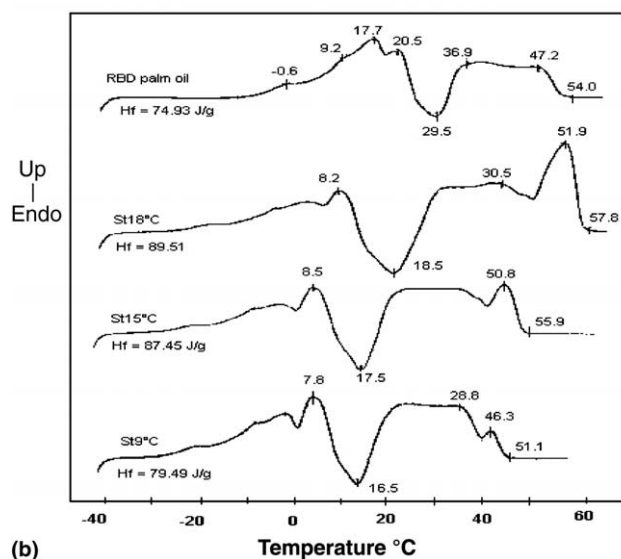
3.4.2. Melting thermograms

The melting thermograms of RBD palm oil (Fig. 5(a)) show more endothermic peaks and shoulders, and an exothermic peak at 27.5 °C due to the poly-morphic changes during the melting process. The olein fractions show fewer endothermic peaks and are totally melted at lower temperatures compared to RBD palm oil. Heats of fusion ΔH_f are also reduced from 74.93 J/g for RBD palm oil to 65.41 J/g for the olein O19 °C.

Fig. 6(a) shows the more complicated melting thermograms of stearin fractions, with an extra peak, at a



(a)



(b)

Fig. 6. (a) DSC cooling thermograms of RBD palm oil and stearin fractions (abbreviations as indicated in Fig. 4(b)). (b) DSC melting thermograms of RBD palm oil and stearin fractions (Abbreviation as indicated in Fig. 4(b)).

higher temperature, observed at 51.9, 50.8 and 46.3 °C for the St18, St15 and St 9 °C samples, respectively. This extra peak could be due to the presence of polysaturated TAGs (SSS) in the stearin fractions and higher ΔH_f is required for its complete melting.

3.5. Crystal morphological observation

Fig. 7 shows the photomicrographs of crystals of RBD palm oil during the cooling process. At the crystallization temperature of 18 °C, small crystals were observed to appear in the liquid oil, as shown in photograph A. At 15 °C, the crystals started to agglomerate to form large crystals (photograph B) and, at 9 °C, the

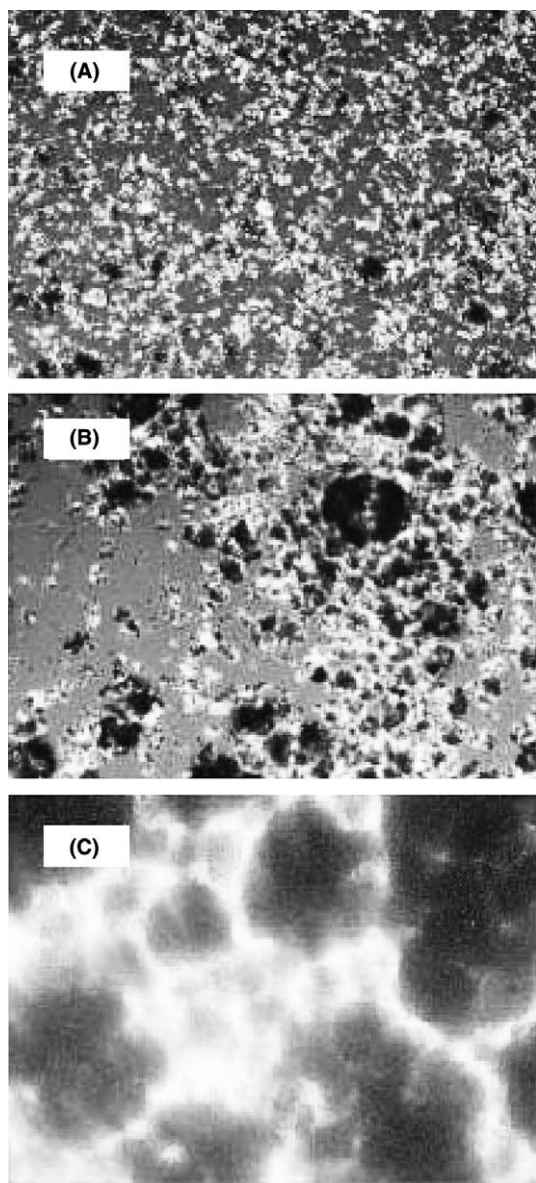


Fig. 7. Photomicrographs of RBD palm oil slurry at different crystallization temperatures during fractionation process at 200 magnification. (A) Crystals at 18 °C. (B) Crystals at 15 °C. (C) Crystals at 9 °C.

crystals became more rounded and spherical as shown in photograph C. The round and spherical-shaped crystals may help to reduce the liquid fraction (olein) from being trapped between crystals during filtration.

4. Conclusion

The crystallization of palm oil is closely associated with its chemical and physical properties. By exploiting

its physical and chemical characteristics, the oil can be separated into a liquid and solid fractions. The production of an olein with IV of more than 63 with good cold stability, i.e., low cloud point would require a proper cooling profile and good separation (filtration). For good separation, the crystals formed must be firm, sandy and uniformly spherical in size. By altering the cooling profile during fractionation process, various types of palm mid-fractions, with varying properties, can be produced.

With a proper understanding of the crystallization process occurring in palm oil, the fractionation process conditions can be optimally controlled to produce required special fractions for specific applications.

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