Effect of Repeated Heating on Thermal Behavior of Crude Palm Oil

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ABSTRACT: Thermal behavior of crude palm oil (CPO) is important to determine the optimal fractionation process and product yield. In this study, the effects of repeated heating on thermal behavior of CPO were examined by differential scanning calorimetry. CPO was heated at 80°C for 5 min, and heating was repeated five times to simulate the common conditions experienced by an oil before reaching the refinery. The result revealed that the thermal behavior of CPO changed after heating. The change, however, occurred only in the behavior of the high-melting stearin peak but not in the low-melting olein peak. Overheating split the stearin peak at 17.30°C to two peaks at 18.88 and 17.30°C and formed a new peak at 11.28°C. Apparently, a new substance has been synthesized.
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KEY WORDS: CPO, DSC, fractionation, repeated heating, thermal behavior.

Crude palm oil (CPO) has been heated several times before it reaches the refinery. Every time CPO has to be removed from a storage tank for transportation, it must be heated up above its melting point (about 37°C) to facilitate pumping of the liquid oil. The frequency of being heated will increase if only a part of the stored CPO is removed. It is recommended that heating does not exceed 55°C (1). However, in practice, it is quite frequently violated. The typical reason for such violations is to shorten the heating time and to avoid claims on demurrage. Storage in tanks that are not equipped with agitators could also induce localized heating. Another reason is to keep the transported CPO in liquid form without heating during transportation because most tankers are not equipped with heating system.

One instrument that can be used to determine thermal properties of materials is the differential scanning calorimeter (DSC). The DSC method has been used in several works related to oils. Hampson and Rothbart (2) used DSC to determine the specific heat of triglycerides. Hagemann and Rothfus (3) used DSC to find out whether polymorph properties of saturated monoacid triglyceride were influenced by the length of odd and even chains. deMan *et al.* (4), D'Souza *et al.* (5), and Herrera and Anon (6) also used DSC to study melting and crystallization of some vegetable oils.

DSC studies on palm oil and palm kernel oil have also been conducted by several workers (7–17). Busfield and Proschogo (7,8) studied heating thermograms of palm stearin and its product of hydrogenation. Their results showed that there was a relationship between thermogram profiles and crystal forms. Che Man and Swe (9) studied the possible cause of poor crystallization of palm oil during fractionation. The cooling thermogram of a palm oil from a failed batch differs from that produced after good crystallization. Yap *et al.* (10) studied polymorphism of palm oil and palm oil products with DSC and X-ray diffraction. The results showed that storage times of palm oil and its products affected their DSC heating curves.

The success of palm oil fractionation determines both quality and yield of the products, namely stearin and olein. Technically, fractionation is done based on the thermal behavior of the oil fractions. Repeated heating could change the major or minor substances in CPO. Such changes will affect thermal behavior of the oil and consequently will affect the selectivity for the optimal fractionation conditions. Therefore, if a common procedure is employed to an overheated oil, it will not provide good selectivity and will cause mixed crystals.

The thermal behavior of CPO is important to determine the optimal fractionation process and product yield. This study was conducted to investigate the effect of repeated heating on thermal behavior of CPO by using DSC thermal analysis.

MATERIALS AND METHODS

Sample. CPO from Ngo Chew Hong Oils and Fats (M) Sdn. Bhd. (Selangor, Malaysia) was used in the experiment.

Thermal analysis by DSC. Information on the instrumentation used and the operating conditions adopted is: calorimeter, Perkin-Elmer (Norwalk, CT) DSC 7, equipped with dry box; cooling system, Perkin-Elmer Intracooler II, with one-stage freon-based mechanical cooler; thermal analysis controller, Perkin-Elmer TAC 7/DX; printer, Hewlett-Packard (Palo Alto, CA) DeskJet 600C; cooling program: T start: 80°C, T final: −50°C, cooling rate: 5°C/min, time at T start: 5

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min, time at T final: 5 min; heating program: T start: –50°C, T final: 80°C, heating rate: 5°C/min, time at T start: 5 min, time at T final: 0 min; nitrogen flow, pure gas for the dry box: 20 psi. The DSC instrument was calibrated with indium and dodecane. A CPO sample of *ca.* 5.4 mg was weighed into an aluminum pan, and the cover was crimped into place. An empty, covered pan was used as a reference. Both were placed in the instrument sample chamber. Heating and cooling cycles were made on the sample.

The sample was subjected to the following temperature program: 80°C isotherm for 5 min, cooled from 80 to –50°C at a rate of 5°C/min, hold at –50°C for 5 min. The same sample was then heated from –50 to 80°C at a rate of 5°C/min. The same sample was run five times under the same conditions. Heating and cooling thermogram profiles were analyzed.

RESULTS AND DISCUSSION

The quality standard of traded CPO is based on the contents of free fatty acids, moisture and impurities, and on the iodine value (20): moisture and impurities, max 0.25%; free fatty acids, max 5%; iodine value, 50–55. For local trading in Malaysia and Indonesia, however, the quality of CPO is subjected to the mutual agreement between buyers and sellers. However, for certification purposes, such standards have to be met.

Thermal behavior of CPO. DSC thermograms for heating and cooling of CPO are presented in Figures 1 and 2, respectively. Table 1 summarizes the temperatures of the exothermic and endothermic peaks that occurred during heating and cooling of CPO.

TABLE 1
Temperature of the Peaks of CPO (°C)[a] on Differential Scanning Calorimetry Curve for Heating and Cooling in Figures 1 and 2

Figure		Heating cycle[b] 1	2	3	4	5	Polymorphic form
				Heating			
1	High-T	—	—	—	44.22	44.85	—
		35.67	35.67	35.67	35.67	35.67	β_1
		18.88	18.88	18.88	19.83	19.83	β'_1
	Low-T	7.27	7.17	6.53	6.53	6.53	α
		5.27	5.27	5.27	5.27	5.27	α'
		1.15	1.15	1.15	1.15	1.15	β'_2
				Cooling			
2	High-T	—	—	—	19.35	19.35	—
		17.30	17.30	17.30	17.30	17.30	β'_1
		—	—	—	11.28	12.23	—
	Low-T	1.78	1.78	1.78	1.78	1.78	α
		–5.50	–5.50	–5.50	–5.50	–5.50	β'_2

[a]Values given are read from right to left.
[b]Heating cycle 1 is associated with A, 2 with B, 3 with C, 4 with D, 5 with E in the respective figures.

The heating thermogram of the CPO before heating showed five peaks: two peaks in the relatively high-temperature (high-T) group and three peaks in the relatively low-temperature (low-T) group. The high-T peaks represent the stearin fraction, while low-T peaks represent the olein fraction. The peaks' directions in the heating thermogram were all upward, indicating that the reactions were endothermic. The heating thermogram showed a sharp and clear separation between the low-T and high-T groups at 14.77°C. The width and height, measured from the saddle point, were 0.8 and 1.8 cm, respectively. A number of research papers have reported on the polymorphic forms of palm oil crystals (11–15). Based on an earlier study by Che Man and Swe (9), polymorphs β'_2, α', α, β'_1, and β_1 of CPO were observed at temperature peaks of 1.15, 5.27, 7.17, 18.88, and 35.67°C.

The cooling thermogram of the CPO before heating showed three peaks: one peak in the high-T group and two peaks in the low-T group. The temperature peaks are presented in Table 1. The peaks' directions were downward, indicating exothermic reactions. The cooling thermogram showed a sharp stearin fraction peak at the first onset temperature of 18.88°C and an offset of 14.45°C. This indicates a good separation ability of the stearin fraction from olein. Enhanced selectivity can be achieved for CPO with a sharp stearin peak.

Effects of repeated heating on thermal behavior of CPO. Heating thermograms. The results showed that there was no significant change in the heating thermogram of CPO that received 80°C heat for 5 min up to three heating cycles (Fig. 1A, B, and C). After the fourth heating cycle, however, the peak at 18.88°C of polymorph β'_1 shifted to 19.83°C and remained at that temperature after the fifth heating cycle.

The temperature peaks indicated that polymorphs β'_2, α', α, and β_1 were unchanged. The start of melting of the stearin fraction was unchanged, and so were the low-T peaks that belong to the olein fraction (Fig. 2A, B, C, and D). The width at the saddle point was relatively unchanged, but its height became shorter, i.e., 1.2 cm, than that of the CPO before heating. This indicates a poorer selectivity of fractionation.

After the fourth heating, a new peak appeared at 44.22°C. The peak shifted a little to 44.85°C after the fifth heating (Fig. 1C and D, and Table 1). Apparently, after four cycles of repeated heating, the nonoil compounds in the CPO were oxidized by the air trapped in the sample pan and generated new compounds that start melting at 42.63°C. Naturally, samples in small quantity are more rapidly oxidized than in bulk. No attempts have been made to correlate temperature and time necessary to meet curve type E in industry; however, Johansson and Pehlergard (1) have made the recommendation not to exceed 55°C. CPO contains 94% triglycerides, 3–5% free fatty acids, and 1% minor and trace components, moisture, and impurities. The minor components are carotenoids, tocopherols, sterols, triterpene alcohol, phospholipids, glycolipids, and terpenic hydrocarbons, while the trace components are triterpene ethers, wax esters, phenolics, and paraffinic hydrocarbons (18). Carotene and free fatty acids are unstable to

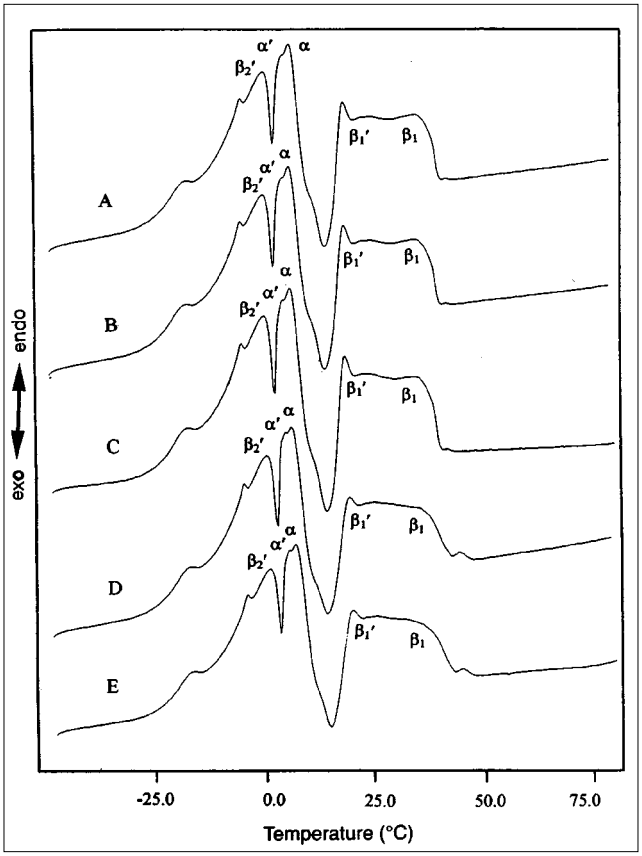

FIG. 1. Differential scanning calorimetry heating thermograms of crude palm oil run at –50 to 80°C at a heating rate of 5°C/min for heating cycles 1 to 5 (A to E).

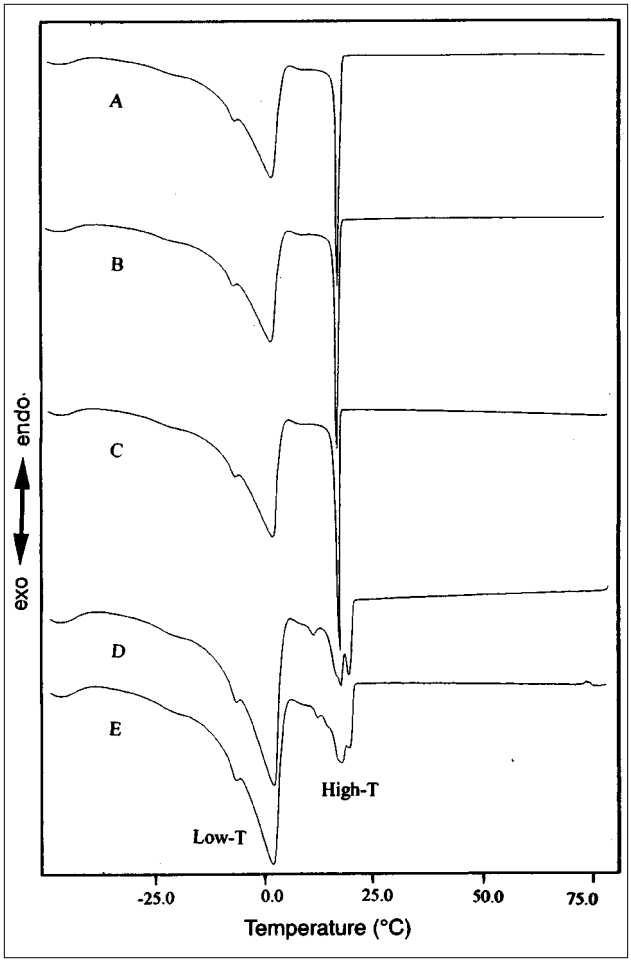

FIG. 2. Differential scanning calorimetry cooling thermograms of crude palm oil run at 80 to –50°C at a cooling rate of 5°C/min for heating cycles 1 to 5 (A to E).

heat, while tocopherol is relatively stable. Therefore, the application of heat will induce the oxidation of these earlier substances and generate new compounds. The possible new compounds formed are hydroperoxides and aldehydes (19). According to Goh *et al.* (18), carotenes are chemically destroyed by the thermal process, and this gave rise to concern because simple compounds, such as toluene, xylenes, ionene and 2,6-dimethylnaphtalene, may be produced. Compared to saturated fatty acids, unsaturated fatty acids are more reactive. Possible reactions include oxidation of carotene, reaction between the oxidation products of carotene and fatty acid chains, reaction between carotene and oxidation products of the fatty acid chains, and reaction between the oxidation products of carotene and the oxidation products of the fatty acid chains. The occurrence of such reactions is suspected to cause the peaks' shifts.

Cooling thermograms. The cooling thermogram (Fig. 2 and Table 1) showed that the change in thermal behavior of CPO appeared after receiving 80°C heat for 5 min after four and five heating cycles. The peak at 17.30°C split into two peaks, i.e., at 17.30 and 19.35°C. The range from the onset to the offset widened from 18.88–14.45°C to 21.41–12.23°C. Similar to the heating thermogram, the low-T peaks in the cooling thermograms were also unchanged. Another significant change was the presence of a new peak at 11.28°C after the fourth heating cycle. The new peak shifted to 12.23°C after the fifth heating cycle. It seemed that heating had induced a reaction of the unsaturated fatty acids and formation of new substances. These new substances are suspected to have a crystallization point at 19.35°C. This observation agrees with the results of the heating thermograms.

Heating to 80°C repeatedly for four heating cycles changed the thermal behavior of CPO. In practice, every time a part of CPO in a storage tank must be pumped out, the whole CPO must be heated. In many cases, CPO is heated more than four times before it reaches the refinery. Overheating shifts the offset of crystallization of the stearin fraction from 14.45 to 12.23°C but does not change the onset of melting at 14.77°C. This indicates the poor selectivity of fractionation so that a poorer stearin fraction may be achieved. Therefore, if a standard fractionation procedure is applied to overheated CPO, there will be more stearin fraction left in the liquid fraction. This will increase the saturated fatty acid content in the olein fraction and will cause cloudiness.

Overheating also split the stearin peak at 17.30°C to two peaks at 17.30 and 19.35°C and formed a new peak at 44.22°C, suggesting that new substances have been synthesized. The presence of new substances will alter characteristics of the stearin produced. It will certainly affect the optimal fractionation process and product yields. This agrees well with Che Man and Swe's finding on failed-batch samples (9).

Normally, the history of CPO reflects on refined–bleached–deodorized palm oil (RBD–PO). Good selectivity in fractionation of RBD–PO depends on agitation, surface area, cooling rate, and most importantly on the thermal profile of the feed oil. Therefore, the common procedure cannot be employed in fractionating such a different RBD–PO. The success of a fractionation process also depends on the crystallizer design. Certain crystallizers provide large cooling surface areas, and therefore, they are suitable for oil with a sharp high-T peak due to their ability to absorb the large amount of latent heat of crystallization. On the other hand, crystallizers with small surface areas are suitable for overheated oil. This agrees well with the findings of Che Man and Swe (9).

This study showed that repeated heating influences the thermal behavior of CPO. The change mainly occurred in the thermal behavior of the stearin peak. However, stearin and olein fractions are still mixed; therefore, such changes will affect the selectivity in the crystallization process.

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