CHEMICAL COMPOSITION AND THERMAL BEHAVIOUR OF TROPICAL FAT FRACTIONS FROM SOLVENT-ASSISTED PROCESS: A REVIEW

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ABSTRACT

Fractional crystallization is a process applied to plant and animal fats to obtain fat products with new functional properties and nutritional values. Fractionation is generally performed through either a dry or a solvent-assisted process. As solvents can wash off the liquid molecules able to entrap the solid component inside, the solvent-crystallization seems to be more efficient than other fractionation procedures. In recent times, fractional crystallization has been investigated for avocado (Persea Americana) butter, engkabang (Shorea macrophylla) fat, palm oil-moringa oil blend, and mee fat (Madhuca longifolia) to prepare solid (stearin) and liquid (olein) fractions. This review sums up the main and recent published studies on chemical and thermal (upon differential scanning calorimetry) properties of fat fractions obtained using solvent-assisted process. It has been argued that the ease of a fat fractionation mainly depends on the thermal characteristics of its triacylglycerol molecules. Fats with low-and high-melting thermal transitions in wide separation would yield fat components with remarkable changes in physico-chemical characteristics, fatty acid and triacylglycerol compositions as well as thermal profiles. The activities involving the use of fat components, during food formulation, may significantly benefit from a further learning of the fats behavior.

1. INTRODUCTION

Modification of lipids plays an important role in the oil and fat processing industry. It has become the integral part of the industry as it helps to widen the product range of the native fats (COSSIGNANI *et al.*, 2008). The main processes available for the lipid modification are: interesterification, fractional crystallization and hydrogenation (O'BRIEN, 2004). Fractional crystallization is the ultimate technique to alter composition and physical properties of fats for a number of reasons. Firstly, preparing a hard component out of native fats via fractional crystallization is more economical than partial hydrogenation. Secondly, fractional crystallization is advantageous over partial hydrogenation because it does not promote trans fatty acids in the finished products (TIMMS, 2005) that are well known to present unfavorable effects on human body (Onacik-Gür *et al.*, 2015). Thirdly, fractional crystallization would contribute to the isolating of fat components of various physical and functional properties through as the so-called "multi-step fractionation" process (DEFFENSE, 1993; TAYLOR, 1976). By overall, the component lipid products isolated are likely to new ingredients suitable for applications where the native fat performs poorly.

Fractionation is generally accomplished by either a dry or a solvent-assisted process (TAYLOR *et al.*, 2000; O'BRIEN, 2004, TIMMS, 2005). The principle of the dry fractionation is based on cooling the oil under controlled conditions slowly and with no solvents (O'BRIEN, 2004). The solvent-assisted fractionation follows a similar principle though, the difference lying in the use of the solvent to ease the crystallization. In the solvent-assisted process the melted native fat was used to mix with a solvent medium and was left to crystallize at a lower temperature. The precipitated fat was filtered off in order to give a high-melting fraction (HMF) while the mother-liquor was evaporated to produce a liquid called low-melting fraction (LMF) (DEFFENSE, 1993; KELLENS et. al, 2007; O'BRIEN, 2004; TAYLOR, 1976; TIMMS, 2005). In recent times, solvent-assisted fractionation has been investigated for a series of tropical fats that include palm oil (MARIKKAR and GHAZALI, 2011), coconut oil (MARIKKAR *et al.*, 2013), cocoa butter (YANTY *et al.*, 2013), engkabang fat (YANTY *et al.*, 2013a), avocado butter (YANTY *et al.*, 2013b), mee fat (MARIKKAR *et al.*, 2010), and lard (YANTY *et al.*, 2011). The current review report has investigated the method of solvent-assisted crystallization, which was effective and sharp while outlining that the yield recoveries of liquid fractions were usually better than those otherwise obtained. Moreover, it was of great concern for getting specialty products such as cocoa butter equivalent, lauric cocoa butter replacers, non-lauric cocoa butter replacers, confectionary products, medium chain triglycerides and high stability liquid oil (O'BRIEN, 2004). As the above mentioned fats and oils are generally known for possessing triacylglycerol (TAG) molecules of different kinds with different melting points, they are found to give lipid components of various kinds through fractionation. In most of these cases, it has been customary to use thermal analysis to cross-check the process and the outcome (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010). Among the various thermal analysis methodologies, differential scanning calorimetry (DSC) has stood out as an important tool for assessing the thermal behavior of oils and fats (VECCHIO *et al.*, 2009; CERRETANI *et al.*, 2012; TAN and NEHDI, 2015). Its use in fat modification studies was shown to give a great deal of information about the fractionation efficiency as well as the fractions thermal characteristics.

The aim of this review is to present an overview of the papers recently published on the chemical composition and thermal properties of the main fractions obtained from fractional crystallization of tropical fats, as the knowledge of these aspects are fundamental for improving the use in food formulation. Properties of avocado (Persea

Americana) butter (AB), engkabang (*Shorea macrophylla*) fat (EF), palm oil-moringa oil blend (PO-MO) and mee fat (*Madhuca longifolia*) (MF) are discussed.

2. MATERALS AND METHODS

2.1. Fractionation

The procedures for obtaining high melting and low-melting components from all the four fats were roughly similar, but with slight variations. Briefly, a portion of the melted sample of individual fat was mixed with acetone in 1:2 (w/v) ratio. The solution was boiled at 60°C until it became uniformly dissolved, and then it was cooled and left at 5±1°C for 2 hr to crystallize. The precipitated fat was filtered off to give a high melting fat fraction called stearin. After removing the precipitate, the mother-liquor was evaporated under reduced-pressure to yield a liquid fraction called olein (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010).

2.2. Analytical methodology

Cloud point (CP), slip melting point (SMP) and iodine value (IV) of the fat samples were determined according to AOCS method Cc.6.25, AOCS method Cc.3.25, and AOCS method Cd Id-92, respectively (AOCS, 1999). The TAG compositional analyses were carried out on a Waters Model 510 liquid chromatography equipped with a differential refractometer Model 410 as a detector (Waters Associates, Milford, MA) using Merck Lichrosphere RP-18 column (5 µm) (12.5 cm × 4 mm i.d.; Merck, Darmstadt, Germany). The mobile phase was a mixture of acetone:acetonitrile (63.5:36.5 v/v) and the flow rate was 1.5 mL/min (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013;YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010). Fatty acid methyl esters analyses were performed on a gas chromatograph (Agillent Technologies, Singapore) fitted with a FID detector using the polar capillary column RTX-5 (0.32 mm internal diameter, 30 m length and 0.25 µm film thickness; Restex Corp., Bellefonte, PA) (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010). Thermal analyses of the samples were carried out on a Mettler Toledo differential scanning calorimeter (DSC 823 Model) equipped with a thermal analysis data station (STARe software, Version 9.0x, Schwerzenbach, Switzerland). Nitrogen (99.99% purity) was used as the purge gas at a rate of ~20 mL/min. Approximately 4-8 mg of molten sample was placed in a standard DSC aluminum pan and then hermetically sealed. An empty, hermetically-sealed DSC aluminum pan was used as the control. The samples were held at 70°C isotherm for 1 min to eliminate the thermal history of the samples, then cooled at 5°C /min to -70°C and held for 1 min. The sample was then brought from -70°C to 70°C at the same rate (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010). In all cases, the temperatures of onset (T_{on}), offset (T_{end}) and at the peak maximum of the melting thermal transitions, recorded during the DSC experiments, were determined using instrument's thermal analysis software.

2.3. Statistical analysis

In all analyses, three replicates were used and the results were expressed as mean value ± standard deviation. Data were statistically analyzed by one-way analysis of variance

(ANOVA), by using Tukey's test of MINITAB™ Statistical Software (MINITAB® Release 14.12.0, New York, USA) at 0.05 probability level.

3. RESULTS AND DISCUSSIONS

3.1. Physico-chemical parameters and potential uses of fractions

3.1.1 High-melting fractions

The physical nature of lipids is particularly relevant when it comes to their functional properties and applications (EL-KALYUOBI *et al.*, 2011). It is hence important to assess the basic physico-chemical parameters such as CP, SMP and IV of fractions. According to Table 1, EF had the highest SMP (37.3°C) value followed by MF (35.5°C), PO-MO (30.5°C) and AB (30°C). As explained in several previous studies (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010), this variation was primarily due to the differences in the melting points of constituent TAG molecules of these fats. An inverse relationship between the SMP values of these fats to their degree of unsaturation was observed (r = -0.9967, p < 0.05). If SMP value of either the native fat or its fractionated components is below the physiological temperature of the human body (37.0ºC), it would make the fat suitable for direct use in food. Because of a lower state of hardness the direct use of the native fat in a formulation was often not found and all this implied a lack of the satisfactory quality attributes. In chocolate products, for instance, the hardness of the fat ingredient plays an important role to keep its texture (EL-KALYUOBI *et al.*, 2011). When compared to normal milk fat, the HMF of milk fat was more compatible with cocoa butter (DEFFENSE, 1993). This links to HMFs generally reporting/showing higher proportions of the saturated TAG components when compared to their respective native samples. According to several previous studies (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010), the high-melting components obtained from fractional crystallization improved in terms of hardness due to higher SMP values [AS (42.5°C), MS (46.5°C), PS (55.5°C) and ES (38.5°C)] (Table 1) as well as elevated solid fat content profiles. NARINE and HUMPHREY (2004) explained that elevated solid fat contents usually helped the high-melting fractions to form stronger fat crystal networks.
Among the HMFs mentioned here, the highest increase of SMP value was noted for PS (25.0 units), followed by AS (12.5 units), MS (11.0 units) and ES (1.3 units). The HMF isolated from AB was AS, which was found to possess higher SMP (42.5 °C) and lower IV (42.8) indicating that it was more or less comparable to those of HMF isolated from PO-MO blend (MARIKKAR and GHAZALI, 2011; MISKANDAR and NOR AINI, 2010). As similar to palm stearin in characteristics, AS might be suitable for fat-based products such as spreads and chocolates. Apart from this, it might also be useful as a fat ingredient in sticks and other solid formulations. According to Table 1, the SMP of MF was 35.5ºC, which was barely similar to those of either cocoa butter (ANON A, 2000) or Borneo Illipe butter (MARIKKAR and YANTY, 2012).

Table 1. Basic physico-chemical characteristics of avocado butter, engkabang fat, mee fat, palm oil-moringa blend, and their fractions[1].

Sample	Iodine value (g I₂/ 100 g)	Slip melting point (°C)	Ref.
AB	84.3±0.1	30.0±0.7	[Yanty *et al.*, 2013b]
AS	42.8±0.1	42.5±0.7	[Yanty *et al.*, 2013b]
AO	103.7±0.2	-	[Yanty *et al.*, 2013b]
MF	61.1±0.4	35.5±0.5	[Marikkar *et al.*, 2010]
MS	47.1±0.1	46.5±0.7	[Marikkar *et al.*, 2010]
MO	64.4±0.5	-	[Marikkar *et al.*, 2010]
PO-MO	54.0±0.5	30.5±0.1	[Marikkar and Ghazali, 2011]
PS	22.5±0.3	55.5±0.1	[Marikkar and Ghazali, 2011]
PO	59.0±1.3	-	[Marikkar and Ghazali, 2011]
EF	30.5±0.7	37.3±0.5	[Yanty *et al.*, 2013a]
ES	28.1±0.6	38.5±0.4	[Yanty *et al.*, 2013a]
EO	44.8±0.6	25.5±0.7	[Yanty *et al.*, 2013a]

[1]Abbreviations: AB, avocado butter; AS, avocado stearin; AO, avocado olein; EF, engkabang fat; ES, engkabang stearin; EO, engkabang olein; PO-MO, palm oil-Moringa oil blend; PS, palm stearin; PO, palm olein; MF, mee fat; MS, mee fat stearin; MO, mee fat olein

According to some reports (MARIKKAR *et al.*, 2010, MARIKKAR and YANTY, 2012), MF can become a halal alternative fat for lard since these two had similar SMP values and their solid content profiles tallied in most temperatures. In a later study, MARIKKAR and YANTY (2011) compared the thermal properties of MS to lard stearin and suggested that MS might have applications such as alternative for lard stearin. Although the SMP value of MS was higher than the physiological temperature, its value was within the range of the palm stearins commercially available (ANON B, 2006). Hence, it might be useful as a raw-material for preparing fat blends simulating commercial shortenings. Similarly, the SMP values of the HMF isolated from the other two fats, namely PO-MO and EF, were also found to be higher than those of their respective native samples. Although the SMP value of ES exceeded the physiological temperature, its value was within the range of the commercially available palm stearin that may be useful as a raw-material in the preparation of either hard margarine or commercial shortenings (ANON B, 2006).

3.1.2 Low-melting fractions

LMFs were softer material when compared to their respective native samples – as the SMP and IV values of Table 1 outline accordingly. In several previous reports (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010), the IV values of the LMFs were higher than their native samples while a situation vice versa was observed for SMP values of LMFs. Among the IV of LMFs, the highest increment was noticed for AO (19.4 units), followed by EO (14.2 units), PO (5.0 units), and MO (3.3 units). In PO-MO, the highest IV was assessed for the LMF obtained under dry-fractionation condition at 18°C and the next lower value was for the LMF obtained under solvent-fractionation condition at 10°C (MARIKKAR and GHAZALI, 2011). However, IV of the LMFs isolated from PO-MO was found to be slightly higher

than palm olein obtained under dry fractionation of palm oil (ANON B, 2006). This could be probably due to the influence of *Moringa* oil factor, which is used to contribute more oleic acid into LMF. When compared to the IV of any other LMFs shown in Table 1, AO revealed a higher IV (103.7). That said, there is a possibility that AO fully maintains its liquid status at low-temperature ranges after longer period of storage. However, AO may be likely to undergo auto-oxidation, as observed in some other liquid oils (RAMLI *et al.*, 2008). AO could be pragmatically useful in lotions since it could give a lighter skin-feel and better skin penetration.

The assessment of SMP of LMFs may be difficult seeing that some of them could remain entirely liquid at lower temperatures. It is, therefore, customary to use CP as it is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance (AOCS, 1999). The CP value of MO was 10.5°C, which was within the range found in most of the commercially available palm olein samples (ANON B, 2006). However, some of the liquid oleins extracted from high-oleic palm oil were found to have CP values as low as 6°C (RAMLI *et al.*, 2008). If its intended use was cooking medium in temperate climatic regions, MO may have some resistance to clouding effect. The LMF of EF was quite different from the other three LMF discussed so far. Although it remains solid at room temperature, its SMP and IV were significantly different from those of the native sample. Hence, this fraction (EO) may not be comparable to the properties of palm olein or any other oleins isolated from any other fatty material straightaway (ANON B, 2006). Alternatively, EO could be used in fat blend preparation suitable for manufacturing soft margarine (MISKANDAR and NOR AINI, 2010).

3.2 Fatty acid compositions of fat fractions

3.2.1 Fatty acid composition of high-melting fractions

The fatty acid distributions of AB, PO-MO, MF, EF, and their fractions have been presented in multiple reports (Table 2). AB, MF, and PO-MO consisted of higher proportions of unsaturated fatty acids (USFA) than saturated fatty acids (SFA), while EF had a higher proportion of SFA than USFA. In AB (YANTY *et al.*, 2013b), oleic (43.7%) was the major fatty acid followed by palmitic acid (30.4%). PO-MO was also found to have oleic (45.5%) as the main fatty acid followed by palmitic acid (38.1%). However, MF and EF had somewhat different fatty acid compositions when compared to the other two fats. In MF, oleic (44.0%) was the major fatty acid followed by stearic acid (22.0%) while in EF, stearic (47.8%) was the major fatty acid followed by oleic acid (32.5%). These differences would definitely have some influence on the crystallization behavior of these fats under the same circumstance/given the same situation/in the same situation.

The HMFs of all fats showed increments in SFA contents due to the migration of the palmitic and steric acids into the solid phase during crystallization. In AS, the percentage of palmitic acid was increase to 59.6% while there was a decrease in the oleic (29.3%) and linoleic acids (5.6%) contents (Table 2). In PS, the increase in the proportion of palmitic acid (68.3%) caused a drop in the proportions of oleic (20.6%) and linoleic acids (3.4%) (MARIKKAR and GHAZALI, 2011). A similar trend was also noted in the fractionation of MF, where SFA content of MS increased tremendously (54.3%) with a concurrent decrease in USFA content (44.1%) (MARIKKAR *et al.*, 2010). However, somewhat different situation was observed in the fractional crystallization of EF where ES reported only very little change in SFA and USFA contents. For instance, the changes in stearic and oleic acid contents were merely 1-2%, which was quite a smaller when compared to the fractional crystallization behaviors of AB, PO-MO, and MF as seen earlier.

Table 2. Fatty acid compositions (%) of avocado butter, engkabang fat, mee fat, palm oil-moringa blend, and their fractions[1].

Sample	Fatty acid (%)	Ref.								
	C 14:0	C 16:0	C 16:1	C 18:0	C 18:1	C 18:2	C 18:3	C 20:0	SFA	USFA	
AB	-	30.4±0.1	5.2±0.0	1.3±0.0	43.7±0.0	17.5±0.1	-	-	31.7	68.3	[Yanty *et al.*, 2013b]
AS	-	59.6±0.1	2.2±0.0	2.9±0.0	29.1±0.1	5.6±0.0	-	-	62.5	37.5	[Yanty *et al.*, 2013b]
AO	-	26.2±0.0	6.1±0.0	1.1±0.0	60.5±0.1	5.9±0.0	-	-	27.3	72.7	[Yanty *et al.*, 2013b]
MF	-	20.9±1.5	-	22.1±0.9	44.0±1.1	7.9±0.8	-	-	43.4	51.6	[Marikkar *et al.*, 2010]
MS	-	25.3±1.3	-	29.0±0.8	38.4±1.6	5.7±0.6	-	-	54.3	44.1	[Marikkar *et al.*, 2010]
MO	-	19.3±1.2	-	16.2±0.7	53.1±0.9	9.6±0.9	-	-	35.5	62.7	[Marikkar *et al.*, 2010]
PO-MO	0.9±0.0	38.1±0.2	0.4±0.0	4.6±0.1	45.5±0.1	8.2±0.0	1.0±0.1	0.5±0.0	45.0	55.1	[Marikkar and Ghazali, 2011]
PS	1.3±0.1	68.3±0.7	-	5.4±0.1	20.6±0.8	3.5±0.2	0.7±0.1	0.4±0.0	75.4	24.6	[Marikkar and Ghazali, 2011]
PO	0.9±0.1	35.2±0.3	0.5±0.0	4.4±0.1	48.3±0.2	8.7±0.0	1.0±0.1	1.0±0.1	41.5	58.5	[Marikkar and Ghazali, 2011]
EF	-	16.6±0.4	-	47.8±0.1	32.5±0.1	1.0±0.0	-	2.1±0.0	66.5	33.5	[Yanty *et al.*, 2013a]
ES	-	16.9±0.2	-	49.1±0.0	30.9±0.0	1.0±0.0	-	2.0±0.1	68.1	31.9	[Yanty *et al.*, 2013a]
EO	-	21.5±0.1	-	24.9±0.0	44.3±0.0	8.3±0.0	-	1.1±0.0	47.5	52.6	[Yanty *et al.*, 2013a]

[1]Abbreviations: AB, avocado butter; AS, avocado stearin; AO, avocado olein; EF, engkabang fat; ES, engkabang stearin; EO, engkabang olein; PO-MO, palm oil-Moringa oil blend; PS, palm stearin; PO, palm olein; MF, mee fat; MS, mee fat stearin; MO, mee fat olein; SFA, saturated fatty acids; USFA, unsaturated fatty acids.

3.2.2 Fatty acid composition of low-melting fractions

The LMFs of all fats experienced increments in the proportions of USFA with the concurrent decreases of SFA contents (Table 2). When TAG molecules with more saturated fatty acids have undergone crystallization easily, the liquid phase would naturally become enriched in unsaturated fatty acids (MARIKKAR and GHAZALI, 2011; YANTY *et al.*, 2013a; MARIKKAR *et al.*, 2010). In AO, oleic acid content was increased from 43.7 to 60.5% while palmitic acid content was decreased from 30.4 to 26.2%. Similar trends of fatty acid changes resulted in LMFs of MF and PO-MO. As PO was the LMF isolated from PO-MO, the oleic acid content increased from 45.6 to 48.3% with the concurrent decrease of palmitic acid content from 38.1 to 35.2%. In MO, oleic acid content increased from 44.0 to 53.1% while there were drops in the proportions of palmitic acid (20.9 to 19.3%) and stearic acid (22.0 to 16.2%). In this case, the decline in stearic acid content was more marked than the decrease of the palmitic acid content. In EO, oleic acid content increased from 32.5 to 44.3% while stearic acid content decreased from 47.8 to 24.9%. In this particular case, however, the palmitic acid content was found to increase from 16.6 to 21.5%. This was considered as an anomalous behavior when compared to the general trend observed in other fats.

3.3 TAG Compositions of fat fractions

3.3.1 TAG composition of high-melting fractions

In multiple reports (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al.*, 2013; YANTY *et al.*, 2013a; YANTY *et al.*, 2013b; MARIKKAR *et al.*, 2010), the comparative TAG distributional profiles of AB, EF, PO-MO, MF and their fractions have been presented. TAG composition of fat fractions is an important determining factor of their chemical properties. Among the native fats, AB, MF, and PO-MO consisted of higher proportions of di-unsaturated TAG molecules while EF had a higher proportion of mono-unsaturated TAG molecules (Table 3). When these fats were subjected to fractional crystallization, the majority of the tri-saturated and di-saturated TAG molecules tended to migrate into the solid phase, leaving mono-saturated and tri-unsaturated TAG molecules in the liquid phase. In AS, for instance, the tri-saturated and di-saturated TAG molecules such as PPP (38.3%) and PPO (30.1%) increased with concurrent decreases in OOL (1.1%), POL (1.6%), and OOO (5.3%). The proportion of PPO in AS was almost equivalent to that of palm mid fraction as reported previously (ANON B, 2006). When MF was fractionated, a similar phenomenon was noticed in TAG composition. In MS, the proportions of di-saturated TAG molecules (MARIKKAR *et al.*, 2010) increased from 42.2 to 73.2% with concurrent reductions in mono-saturated (18.2%) and tri-unsaturated (4.9%) TAG molecules. TAG molecular species such as POP, POS, and SOS experienced increments while PLO, OOO, OOP, and OOS experienced decreases (MARIKKAR *et al.*, 2010). The proportion of SPO in MS was almost equivalent to that of cocoa butter as reported previously (SIMONEAU *et al*, 1999; ANON A, 2000). In the fractionation of PO-MO, migration of PPP into the solid phase was considerable. Similar observations were also made by other researchers in the dry fractionation of palm oil, as reported previously (MISKANDAR and NOR AINI, 2010; RAMLI *et al.*, 2008). As a result, tri-saturated TAG molecules of PS was increased from 7.1 to 50.4% with concurrent reductions in mono-saturated (9.0%) and tri-unsaturated TAG molecules (2.2%) (Table 3).

Table 3. Triacylglycerol (TAG) compositions (%) of avocado butter, engkabang fat, mee fat, palm oil-moringa blend, and their olein and stearin fractions[1].

TAG	AB	AS	AO	MF	MS	MO	PO-MO	PS	PO	EF	ES	EO
LLLn	1.9±0.0	-	2.7±0.1	-	-	-	-	-	-	-	-	-
LLL	0.9±0.1	0.5±0.0	1.2±0.1	-	-	-	-	-	-	-	-	-
OLL	3.2±0.0	0.5±0.0	6.0±0.1	-	-	-	-	-	-	-	-	-
OOA	-	-	-	-	-	-	-	-	-	-	-	1.7±0.1
OOL	9.0±0.0	1.1±0.0	17.0±0.2	3.0±0.3	1.5±0.0	2.6±0.1	1.6±0.1	0.3±0.1	2.0±0.0	-	-	0.4±0.0
OOO	11.4±0.0	5.3±0.0	22.4±0.4	9.9±0.2	3.5±0.0	12.6±0.1	10.0±0.2	1.9±0.2	9.9±0.5	0.1±0.0	0.4±0.0	3.3±0.1
OOSt	0.5±0.0	0.6±0.1	1.1±0.1	17.8±0.0	7.4±0.1	24.1±0.0	4.6±0.6	0.5±0.1	4.1±0.2	1.4±0.0	1.3±0.1	29.7±0.2
OPO	22.8±0.0	12.3±0.0	8.8±0.2	22.9±0.9	9.0±0.0	28.6±0.1	24.1±1.4	6.1±0.0	26.1±0.1	0.7±0.0	0.4±0.0	16.0±0.4
MMM	-	-	-	-	-	-	0.4±0.0	-	0.2±0.0	-	-	-
MPL	-	-	-	-	-	-	0.2±0.1	-	0.2±0.0	-	-	-
PLL	4.2±0.0	0.2±0.0	5.6±0.1	-	-	-	1.5±0.0	0.3±0.1	2.1±0.3	-	-	0.3±0.0
POL	19.3±0.1	1.6±0.0	13.2±0.2	4.3±0.4	1.8±0.0	2.6±0.2	8.9±0.4	2.1±0.1	10.8±0.1	-	-	1.7±0.2
POSt	-	-	-	-	-	-	-	3.4±0.2	5.2±0.1	35.6±0.1	38.2±0.1	12.3±0.2
PPL	4.0±0.1	1.7±0.1	0.2±0.0	1.2±0.0	0.4±0.0	Tr.	6.9±1.4	6.1±0.1	10.1±0.0	0.2±0.0	0.1±0.0	3.1±0.1
PPO	12.4±0.1	30.1±0.4	0.2±0.0	11.9±0.7	14.0±0.1	12.1±0.0	29.8±1.8	28.9±0.1	28.71±0.1	7.3±0.0	7.3±0.0	16.5±0.3
PPP	2.9±0.1	38.3±0.5	0.6±0.0	Tr.	0.2±0.1	Tr.	6.0±1.2	42.1±0.2	0.4±0.0	-	-	-
PPSt	0.1±0.0	4.0±0.1	-	Tr.	1.8±0.0	Tr.	0.7±0.2	8.3±0.1	-	0.3±0.0	0.2±0.0	1.0±0.1
StOA	-	-	-	-	-	-	-	-	-	3.8±0.1	3.7±0.2	-
StPO	0.6±0.0	1.7±0.0	-	19.3±0.4	35.1±0.0	14.1±0.0	5.4±0.1	-	-	-	-	-
StStO	-	-	-	9.7±0.6	23.8±0.0	3.5±0.2	-	-	-	50.0±0.1	47.8±0.3	2.7±0.3
StStSt	-	-	-	-	-	-	-	-	-	0.3±0.0	0.3±0.0	-
Others	6.8±0.0	2.3±0.9	21.0±1.6	-	1.9±0.1	-	-	-	-	0.4±0.0	0.2±0.0	11.4
SSS	3.5	42.3	0.6	-	2.0	-	7.1	50.4	0.6	0.6	0.6	1.0
USS	17.0	33.5	0.4	42.2	73.2	30.2	42.3	38.4	42.2	96.8	97.1	34.6
UUS	46.8	14.7	28.7	45.0	18.2	55.3	39.0	9.0	43.01	2.1	1.7	49.4
UUU	26.4	7.4	49.3	12.9	4.9	15.2	11.6	2.2	11.94	0.1	0.4	3.7
Ref.	[Yanty et al., 2013b]	[Yanty et al., 2013b]	[Yanty et al., 2013b]	[Marikkar et al., 2010]	[Marikkar et al., 2010]	[Marikkar et al., 2010]	[Marikkar and Ghazali, 2011]	[Marikkar and Ghazali, 2011]	[Marikkar and Ghazali, 2011]	[Yanty et al., 2013a]	[Yanty et al., 2013a]	[Yanty et al., 2013a]

[1]Abbreviations: O, oleic; P, palmitic; L, linoleic; Ln, linolenic; St, stearic; Tr., trace; UUU, triunsaturated; UUS, diunsaturated; USS, disaturated; SSS, triunsaturated. For other abbreviations see Table 1.

In contrast to the three native fats discussed so far, a different situation was noticed in the fractionation of EF (YANTY *et al*., 2013a). This could be due to the fact that EF was a fat dominated by stearic acid enriched TAG molecules (NESARETNAM and MOHD ALI, 1992) while others were dominated by palmitic and oleic enriched TAG molecules. This fact was further confirmed in a separate study carried out by NUR ILLYIN and co-workers (2013) who used EF as one of the raw materials to formulate a fat substitute for lard. Although there was an increase in the proportion of di-saturated TAG molecules of ES with decreasing proportions of mono-saturated TAG molecules, the changes were not remarkable. Interestingly, StOSt and POSt together accounted for 86% of all TAG molecules of ES.

3.3.2 TAG composition of low-melting fractions

TAG composition of LMFs isolated from AB, PO-MO, MF and EF are presented in Table 3. LMFs of these fats were generally found to possess higher proportions of di-unsaturated and tri-unsaturated TAG molecules. For instance, AO was found to possess higher percentages of OOO (22.4%) and OOL (17.0%) with respect to the native AB sample. The increased proportions of di-unsaturated and tri-unsaturated TAGs in AO were compatible to the increased amounts of oleic and linoleic acids of AO, as noticed in the fatty acid distribution (Table 2). MO also had remarkably higher proportions of di-unsaturated and tri-unsaturated TAG molecules. In this case, TAG molecular species such as OOO, OOP and OOS experienced increments while TAG species such as POS and SOS underwent decreases. PO (MARIKKAR and GHAZALI, 2011) consisted of di-unsaturated (43.0%), di-saturated (42.2%) and tri-unsaturated (11.9%) TAG molecules. This was somewhat similar to the findings reported previously for dry fractionation of palm oil (MISKANDAR and NOR AINI, 2010, RAMLI *et al*., 2008). In EO, the TAG molecular species namely SOO and POO experienced increments while TAG species such as POS and SOS have undergone decreases. The relative increase in the proportions of di-unsaturated and tri-unsaturated TAG molecules would have led to the increase of oleic acid content as noticed earlier (Table 2). By overall, the changing nature of TAG composition in the LMF caused an increase in the iodine value of AO (103.7), MO (64.4), PO (59.0), and EO (44.8) (Table 1) (MARIKKAR and GHAZALI, 2011; YANTY *et al*., 2013a; MARIKKAR *et al*., 2010).

3.4. Thermal behaviors of fat fractions

3.4.1 Thermal behavior of high-melting fractions

The DSC thermal profiles of AB, PO-MO, MF, and EF have been documented in multiple reports (MARIKKAR and GHAZALI, 2011; MARIKKAR *et al*., 2013; YANTY *et al*., 2013a; YANTY *et al*., 2013b; MARIKKAR *et al*., 2010). Past research (MARIKKAR *et al*., 2013; RAMLI *et al*., 2008) has shown that DSC thermal profiles have greatly contributed to the understanding of the fractional crystallization behavior of individual fats. Particularly, the distribution of thermal transitions in these fats provided some important basis for predictions of the outcome of fractionation of individual fat (CHE MAN *et al*, 1999). This was also confirmed in several studies conducted on dry fractionation of palm oil (RAMLI *et al*., 2008; ZALIHA *et al*., 2004). According to Figs. 1-4, native samples of AB, PO-MO, and MF displayed cooling curves with a low-melting thermal transition below 0°C and a high-melting thermal transition above 0°C. Likewise, the melting curves of these three fats were also found to have two well-separated endothermic transitions, which represented the low- and high-melting regions. This phenomenon was well-evidenced in the thermal studies of palm oil reported by other investigators (CHE MAN *et al*, 1999; YANTY *et al*.,

2012; SHUKAT *et al*., 2012; SAMI *et al*., 2012). As EF had a somewhat different composition in terms of fatty acid (Table 2) and TAG (Table 3) distributions, its cooling curve was different from those of AB, PO-MO and MF. It had a strong single major exothermic thermal transition at 16.40°C with minor thermal transitions at 8.6°C and -9.2°C. According to previous reports (YANTY *et al*., 2013a; NUR ILLYIN *et al*., 2013), co-crystallization of TAG molecular species within a narrow temperature region would have caused EF to display a single major thermal transition.

The thermal behaviors of HMFs were presented in Figs. 1-4. Depending on the fatty acid and TAG compositions, the nature of cooling and heating curves displayed by individual HMF was found to vary. This was in accordance with the findings reported previously for whole lipids in other studies (MARIKKAR *et al*., 2011; LONG *et al*., 2005). As shown in Fig. 1A (Curve 3), the thermal curve of AS had a strong high-melting thermal transition with duplet at 40.5°C [peak C_1] and 32.5°C [peak C_2].
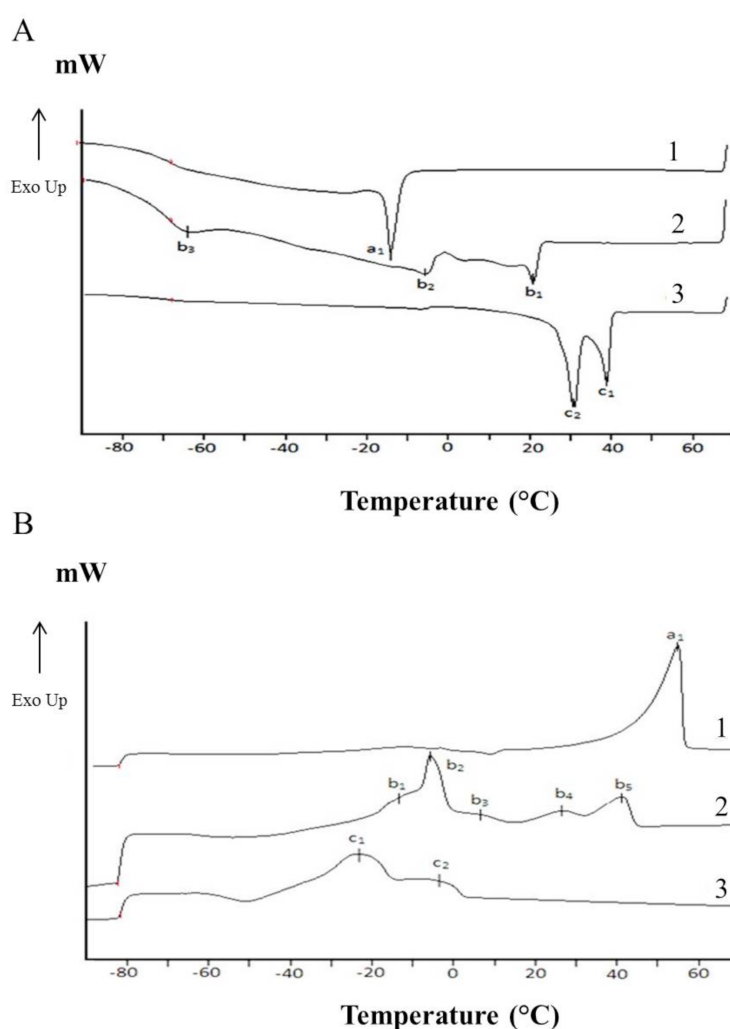

Figure 1. (A) DSC cooling curves of avocado fat (curve-2), avocado olein (curve-1), and avocado stearin (curve-3) and (B) DSC heating curves of avocado fat (curve-2), avocado stearin (curve-1), and avocado olein (curve-3).

This curve did not show any low-melting transition below 10.0ºC, mainly due to the fact that it had lost most of the di-and tri-unsaturated TAG molecules during fractional crystallization. This was commonly noticed in several previous studies related to the dry fractionation of palm oil (MISKANDAR and NOR AINI, 2010, CHE MAN *et al.*, 1999). With respect to the cooling curve of native sample, T_{on} and the peak maximum of thermal transitions shifted toward the high-temperature region (Table 4). These changes were positively correlated (r = +0.996, p < 0.0001) with increasing proportions of disaturated and trisaturated TAG molecular species of AS (Table 3) as well as SFA of AS with respect to that of the native sample (Table 2).

According to O'BRIEN (2004), these groups of TAG molecules were generally found to have higher melting temperatures. The fractionation behavior of MF (Fig. 2) was slightly different from those of AB and PO-MO since it had more stearic acid esterified to TAG molecular species (Table 3). The cooling curve representing MS (as shown in Fig. 2A, curve 3) was distinguishable from that of the native sample as the high-melting thermal transition (peak c_i) of the curve became more dominant with the gradual reduction of the low-melting transition (peak c_3). As seen before with HMFs of AB and PO-MO, the positions of thermal transitions of MS in the cooling curve also shifted towards higher temperatures (Tables 4 and 5), owing to the decline of TAG with high degree of unsaturation. In fact, the changing DSC thermodynamic parameters were well-correlated with the changing proportion of di-unsaturated and tri-unsaturated TAG groups in the fractions (Table 3).
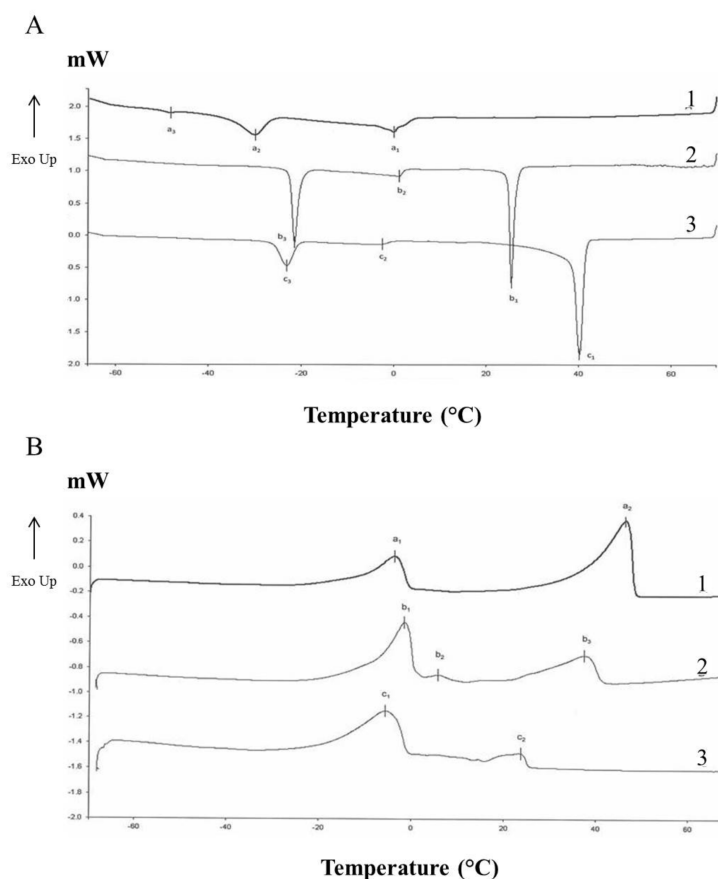

Figure 2. (A) DSC cooling curve of Mee fat (curve-2), Mee olein (curve-1) and Mee stearin (curve-3) and (B) DSC heating curves of Mee fat (curve-2), Mee stearin (curve-1) and Mee olein (curve-3).

The melting curve representing MS, as shown in Fig. 2B (curve 1), was distinguishable from that of the native sample as its high-melting thermal transition has become more dominant than the low-melting transition. It had its major transition at 46.3ºC (a_2) with a minor transition at -3.7ºC (a_3).

Table 4. Thermal parameters associated with the cooling curves of avocado butter, mee fat, engkabang fat, palm oil-moringa oil blend, and their olein and stearin fractions[1].

| Sample	T_{On} (°C)	Tran1 (°C)	Tran2 (°C)	Tran3 (°C)	Ref.
AB	23.9±0.2	22.2±0.0	-2.7±0.1	-64.4±0.2	[Yanty *et al.*, 2013b]
AS	41.3±0.0	40.5±0.1	32.5±0.1	-	[Yanty *et al.*, 2013b]
AO	2.5±0.2	-12.9±0.1	-	-	[Yanty *et al.*, 2013b]
MF	29.6±0.0	25.4±0.0	1.2±0.2	-21.4±0.0	[Marikkar *et al.*, 2010]
MS	42.4±0.1	40.2±0.1	-2.2±0.0	-23.2±0.0	[Marikkar *et al.*, 2010]
MO	5.2±0.2	0.0±0.0	-30.0±0.1	-47.3±0.3	[Marikkar *et al.*, 2010]
PO-MO	20.4±0.2	18.8±0.1	0.7±0.0	-	[Marikkar and Ghazali, 2011]
PS	44.4±0.1	42.8±0.3	-	-	[Marikkar and Ghazali, 2011]
PO	2.8±0.1	0.5±0.0	-	-	[Marikkar and Ghazali, 2011]
EF	17.6±0.1	16.4±0.2	8.6±0.1	-9.2±0.1	[Yanty *et al.*, 2013a]
ES	19.0±0.0	17.2±0.0	8.9±0.1	-7.8±0.1	[Yanty *et al.*, 2013a]
EO	16.8±0.0	17.0±0.1	7.2±0.1	-	[Yanty *et al.*, 2013a]

[1]Abbreviation: T_{On}, Onset of crystallization; Trans, thermal transition. For other abbreviations see Table 1.

Table 5. Thermal parameters associated with the melting curves of avocado butter, mee fat, engkabang fat, palm oil-moringa oil blend, and their olein and stearin fractions[1].

Sample	Tran1 (°C)	Tran2 (°C)	Tran3 (°C)	Tran4 (°C)	Tran5 (°C)	T_{End} (°C)	Ref.
AB	-12.2±0.0	-5.5±0.0	7.6±0.1	26.6±0.1	41.3±0.4	44.7±0.1	[Yanty *et al.*, 2013b]
AS	55.2±0.2	-	-	-	-	57.1±0.0	[Yanty *et al.*, 2013b]
AO	-24.0±0.3	-2.1±0.3	-	-	-	3.4±0.0	[Yanty *et al.*, 2013b]
MF	-1.5±0.1	5.6±0.1	37.7±0.1	-	-	38.9±0.1	[Marikkar *et al.*, 2010]
MS	-3.7±0.2	46.3±0.2	-	-	-	49.8±0.4	[Marikkar *et al.*, 2010]
MO	-5.4±0.1	23.8±0.1	-	-	-	26.2±0.2	[Marikkar *et al.*, 2010]
PO-MO	1.3±0.1	5.2±0.1	21.5±0.0	42.1±0.1	-	39.3±0.2	[Marikkar and Ghazali, 2011]
PS	51.4±0.0	63.3±0.2	-	-	-	66.4±0.1	[Marikkar and Ghazali, 2011]
PO	6.3±0.2	10.1±0.3	-	-	-	15.3±0.0	[Marikkar and Ghazali, 2011]
EF	17.0±0.0	20.3±0.1	26.6±0.2	33.7±0.0	-	35.3±0.1	[Yanty *et al.*, 2013a]
ES	-	-	27.1±0.1	-	-	37.5±0.0	[Yanty *et al.*, 2013a]
EO	-10.5±0.1	5.3±0.0	19.2±0.1	-	-	28.1±0.1	[Yanty *et al.*, 2013a]

[1]Abbreviation: Trans, thermal transition; T_{End}, end of melting temperature. For other abbreviations see Table 1

The fractional crystallization behavior of PO-MO was expected to be similar to that of AB since both of these were found to possess TAG molecular species predominantly esterified by oleic and palmitic acids. The cooling curve of PS, as shown in Fig. 3A (curve 3), was found to possess a high-melting thermal transition only at 29.25°C (peak c_i) with no strong low-melting transition appearing in the low-temperature region.
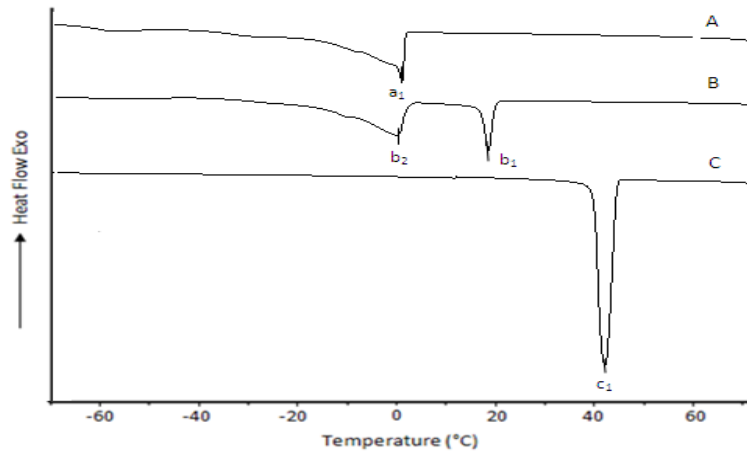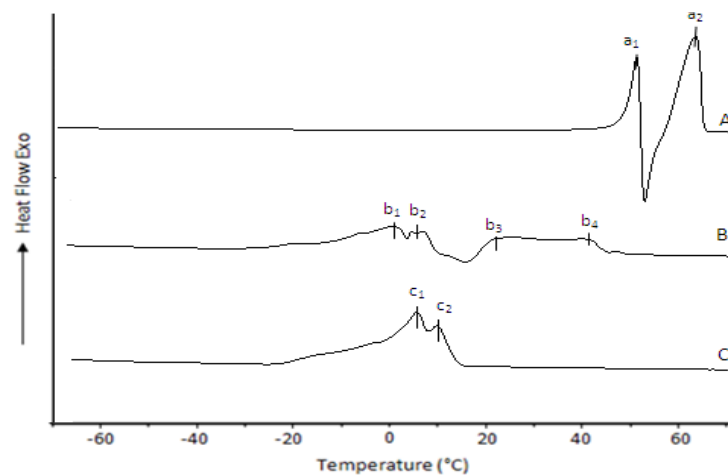

Figure 3. (X) DSC cooling curves of palm olein (curve-A), palm oil (curve-B), and palm stearin (curve-C) and (Y) DSC heating curves of palm stearin (curve-A), palm oil (curve-B), and palm olein (curve-C).

As reported by other researchers (MISKANDAR and NOR AINI, 2010; CHE MAN *et al.*, 1999; ZALIHA *et al.*, 2004) about the PS cooling curve, this phenomenon was frequently attributed to the occlusion of small amount of liquid oil within the crystal matrix during the crystallization process. This difference was primarily due to the high-fractionation efficiency of solvent-assisted processes when compared to dry fractionation technique. As mentioned previously, the use of solvent in fractionation helped to wash away the small amount of liquid oil occluded within the crystal matrix (MARIKKAR and GHAZALI, 2011). As the overall cooling profile of PS shown in Fig. 3A (curve 3) was slightly different with respect to that of native palm stearin, some differences could be expected in the onset

of crystallization temperatures as well as the position of the thermal transitions. These changes were mainly due to differences in the conditions adopted during commercial fractionation (MISKANDAR and NOR AINI, 2010, CHE MAN *et al.*, 1999; ZALIHA *et al.*, 2004). The DSC thermodynamic parameters were positively correlated ($r = 0.986$, $p < 0.001$) to the increasing proportions of di-saturated and tri-saturated TAG molecular species in PS (Table 3). This was also positively correlated to the increasing proportion of the SFA of PS with respect to that of the native sample (Table 2).

The fractionation behavior of EF was completely different from those of AB, PO-MO and MF. As discussed before, this anomalous behavior was mainly due to the nature of the composition of EF resulting from the combination of TAG molecules esterified with more stearic fatty acid (Tables 2 and 3). The cooling curve of ES as shown in Fig. 4A (curve 3) displayed a major sharp transition at 17.15°C (peak c_1) with two minor thermal transitions at 5.7°C (peak c_2) and -5.2°C (peak c_3) (Table 3) while its melting curve displayed the major transition at 27.05°C (peak a_1, Fig. 4B, curve 1) (Table 4). In the melting curve, the end set temperature of melting of ES was slightly higher than that of the native sample. By overall, ES showed significant changes in the values of T_{on}, T_{end} as well as rest of the DSC parameters of both cooling and heating curves.
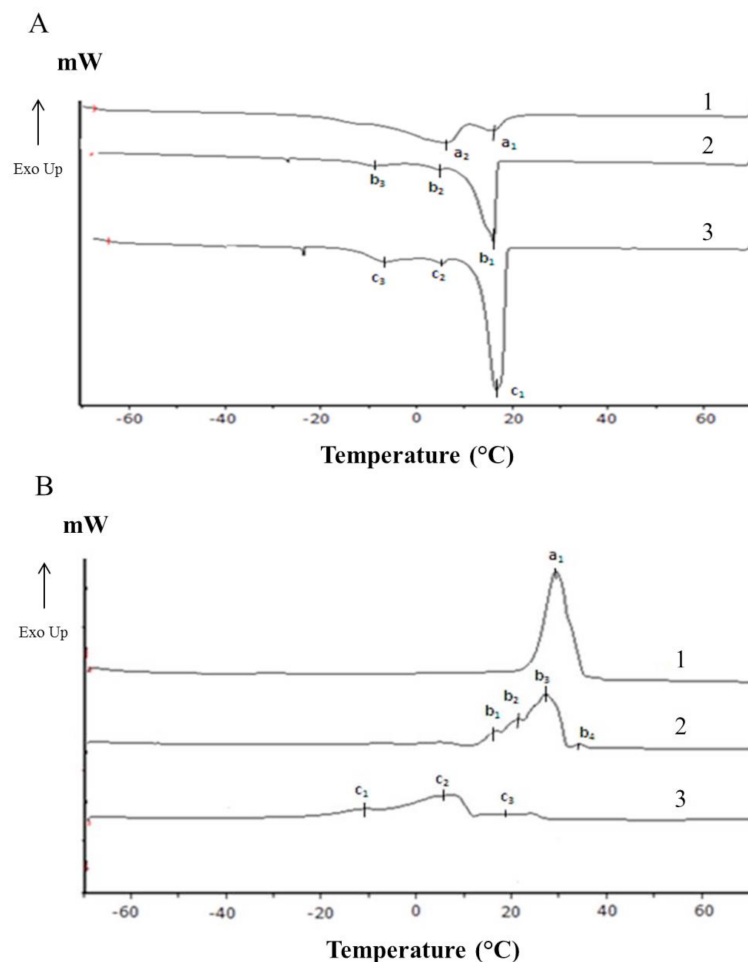

Figure 4. (A) DSC cooling curves of engkabang olein (curve-1), engkabang fat (curve-2), and engkabang stearin (curve-3) and (B) DSC heating curves of engkabang stearin (curve-1), engkabang fat (curve-2), and engkabang olein (curve-3).

3.4.2 Thermal behavior of low-melting fractions

Thermal behaviors of LMFs were quite different when compared to their respective native fats. According to several previous reports, this has been true even for dry fractionation of palm oil and milk fat (TIMMS, 2005; DEFFENCE, 1993; RAMLI *et al.*, 2008; CHE MAN *et al.*, 1999; ZALIHA *et al.*, 2004; LONG *et al.*, 2005). Owing to migration of highly saturated TAG molecules into the solid phase, they were largely composed of TAG molecules esterified with more unsaturated fatty acids (Tables 2 and 3). These TAG molecules would make LMFs to have low solid fat and display low-melting points (DE MAN, 1999). Since they contain lesser amounts of high-melting TAG groups, their cooling and melting curves tend to differ from those of their native fats by not having any major thermal transition in the high-temperature region of the DSC cooling curve (Figs. 1-4). This phenomenon was evidently seen in liquid palm olein isolated from dry fractionation of palm oil (RAMLI *et al.*, 2008; ZALIHA *et al.*, 2004; MARIKKAR *et al.*, 2011) and palm oils enriched with diacylglycerols (LONG *et al.*, 2005). The cooling curve of AO [Fig. 1 (A); Curve 1] isolated from AB was found to display thermal transitions in the lower-temperature region with peak maximum at -12.9°C (peak a_1). Hardly, any significant thermal transition was noticed in the temperature region above 2.5°C. Likewise, the melting curve of AO shown in (Fig. 1 B) also displayed a broad thermal transition in the lower-temperature region with peak maximum at -24.0°C (peak c_1) and -2.10°C (peak c_2), but hardly any significant thermal transition in the temperature region above 2.5°C. With respect to the native fat, the peak maxima of thermal transitions in both cooling and melting curves were also found to shift toward the low-temperature region (Tables 4 and 5). This changing pattern of DSC thermodynamic parameters was also positively correlated to the increasing proportion of the USFA and di-and tri-unsaturated TAG molecules of AO (Tables 2 and 3) ($r = 0.974$, $p < 0.001$). The shifting of thermodynamic transitions of low-melting fractions is a common phenomenon even noted in commercial dry fractionation of crude palm oil (CHE MAN *et al.*, 1999; ZALIHA *et al.*, 2004).

The cooling and melting curves of the LMF of MF are depicted in Fig. 2. As shown in Fig. 2 (A), the DSC cooling curve of MO had its major exothermic transitions at 0°C (peak a_1) and -30.0°C (peak a_2) and its onset of crystallization was at 5.2°C, which was slightly higher than that of AO. This could be attributed to the difference in SFA (%) contents of MO and AO (Table 2). Past studies already showed that onset temperatures of crystallization of LMF of palm oil from different suppliers were found to vary with the changes in fatty acid (MARIKKAR *et al.*, 2011). According to Fig. 2 (B), the DSC melting curve of MO had its major thermal transition in the lower-temperature region at -5.4°C (peak c_1) while a minute high-melting transition appeared at 23.8°C (peak c_1) (Table 4). This was an indication that MO has lost majority of the high-melting TAG molecules during fractionation. According to Table 3, there was 12% drop in the proportion of di-saturated TAG molecules after fractionation. TAN and NEHDI (2015) earlier discussed the co-relationship between DSC thermodynamic parameters and chemical composition of plant oils, and the same co-relationship was also found to hold true in the case of fractions isolated from tropical fats selected in this study.

The LMF isolated from PO-MO also exhibited a similar trend as seen before in AO and MO. According to Fig. 3(A), PO did not show the sharp high-melting transition possessed by the native sample. The onset temperature of crystallization of PO was 2.8°C (Table 4) and there was hardly any exothermic thermal transition in the temperature region above this point. By overall, this characteristic feature was comparably similar to those of palm olein samples reported previously by other researchers (CHE MAN *et al.*, 1999; MARIKKAR *et al.*, 2011). According to Fig. 3(B), the melting curve of PO displayed dual melting thermal transitions at 6.3°C (peak c_1) and 10.1°C (peak c_2) and the end of melting

was at 15.3°C. These values were slightly different from those of palm olein reported previously by ZALIHA *et al* (2004) and CHE MAN *et al* (1999). This deviation could be attributed to the influence of fractionation conditions adopted in the two different fractionation approaches. Particularly, the starting material used in the former was palm oil while the starting material used in the later was PO-MO blend.

A totally different result could be observed with respect to the LMF of EF. As shown in Fig. 4A, EO did not show any significant low-melting transition in the negative temperature region, but instead it displayed a broad thermal transition with a doublet having peak maxima at 17.0°C (peak a_1) and 7.2°C (peak a_2). This was quite an anomalous behavior when compared to the thermal behavior noticed in the cooling curves of AO, PO, and MO. The native sample of EF itself did not display any strong low-melting transition in the low-temperature region of the DSC cooling curve (YANTY *et al.*, 2013a). As mentioned before EF was a fat containing TAG molecules, esterified mostly with stearic acid (Table 3). These were the group of TAG molecules reappearing in the TAG composition of EO. Apart from the changing pattern of the thermal transitions, there were significant changes in the onset temperature of crystallization as well as the other DSC parameters. As already noted with the LMFs of AB, PO-MO, MF etc., the onset temperature of crystallization of EO was also found to decrease with respect to the native sample (Table 3). As shown in Fig. 4B (curve 3), the melting curve of EO displayed the major thermal transition at 5.3°C (peak c_2) with a shoulder peak at - 10.5°C (peak c_1) and a minor transition at 19.2°C (peak c_3). Similar to the cooling curve pattern seen before, the melting behavior pattern was completely different from that of the native sample (curve 2). In addition, EO had its end of melting at 28.1°C, which was quite lower when compared to that of the native sample (Table 5).

4. CONCLUDING REMARKS

The current study compared the fractional crystallization behavior differences of AB, PO-MO, MF, and EF using the analytical data obtained from GLC, HPLC and DSC techniques. Since the thermal characteristics of oils and fats are generally related to their TAG composition, the outstanding differences in the thermal profiles of the LMF and HMF fractions were well-related to the changing TAG composition and to the degree of the fatty acids unsaturation. The HMF fractions of all fats experienced increases in the percentage of saturated fatty acids, while increases in the proportions of unsaturated fatty acids resulted in the LMF fractions of all fats. The iodine value differences among them clearly showed that the HMF and LMF fractions underwent changes in their fatty acid and TAG compositions. Due to the fatty acid and TAG compositional differences, the fractions isolated through crystallization are new products with differing functional properties. The HMF fractions of these fats tended to emerge from the high-melting TAG molecular species of native fats. The reason lies in the fact that these TAG molecular species are usually represented by relatively more saturated TAG molecules, which would undergo solidification rapidly. While the LMF fractions obtained can be generally used as cooking and frying oils, the HMF fractions may be considered as a raw ingredient for preparing sticks, hard margarine, commercial shortening and other solid formulations because of their hard nature and higher SMP values. The fractionation at times yielded exotic specialty fat products, such as palm mid-fraction, that could be used as cocoa butter substitute. In some instances, fractionation helped to come out with confectionary fats and oils with higher oxidative stability. In conclusion, it should be noted that the fractional crystallization approach is a mere physical process with a low environmental impact, therefore it provides several advantages over other methods of fat derivative formation.

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