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CHANGES ON THE SOLID FAT CONTENT OF PALM OIL/SUNFLOWER OIL BLENDS VIA INTERESTERIFICATION

(Perubahan Kandungan Lemak Pepejal Campuran Minyak Sawit RBD/Bunga Matahari Melalui Penginteresteran)

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Abstract

Physicochemical characteristics of binary blends containing refined-deodorized-bleached palm oil (RBDPO) and sunflower oil (SFO) were studied before and after chemical interesterification at different temperature (110 ^{o}C (CIE1) and 80 ^{o}C (CIE2)) using sodium methoxide as catalyst. Thirty-three samples with different ratios were analyzed for triacylglycerol (TAG) composition, fatty acid composition (FAC) and solid fat content (SFC) profile. Upon CIE, extensive rearrangements of fatty acids among triacylglycerol (TAG) were seen. Generally, CIE not induced enormous changes in the TAG compositions of ratio 8:2 and 5:5 of RBDPO:SFO blends. However, CIE induced enormous changes in the TAG compositions of the 9:1, 7:3, 6:4, 4:6, 3:7, 2:8 and 1:9 blends, which some of the TAGs were increasing while the other decreasing. These changes in TAG profiles resulted in some changes in the physical properties (especially SFC) of the blends. Generally, the SFC of interesterified blend were decreased after CIE1 and increased after CIE2, except for sample 10:0, 8:2, 7:3, 5:5 and 9:1 which were decreased after CIE1 and CIE2. As a conclusion, CIE1 and CIE2 successfully changed the physicochemical characteristics of the binary blends.

Keywords: palm oil, sunflower oil, interesterification, blending, solid fat content

Abstrak

Ciri-ciri fiziko-kimia adunan duaan langsung minyak sawit tertapis, terluntur dan ternyahbau/minyak bunga matahari (RBDPO/SFO) dikaji sebelum dan selepas penginteresteran kimia pada suhu berbeza (110 ^{o}C (CIE1) dan 80 ^{o}C (CIE2)) dengan menggunakan mangkin natrium metoksida. Sebanyak 33 adunan dengan nisbah yang berbeza dianalisis menggunakan kaedah penentuan komposisi triasilgliserol (TAG), komposisi asid lemak (FAC) dan kandungan lemak pepejal (SFC) yang dilakukan sebelum dan selepas penginteresteran kimia. Penyusunan semula asid-asid lemak pada molekul-molekul TAG dikesan selepas penginteresteran kimia. Umumnya, penginteresteran kimia merangsang perubahan yang tidak begitu ketara di dalam komposisi TAG adunan 8:2 dan 5:5. Walaubagaimanapun, penginteresteran kimia telah merangsang perubahan yang agak besar bagi adunan 9:1, 7:3, 6:4, 4:6, 3:7, 2:8 dan 1:9 dengan beberapa jenis TAG meningkat, manakala yang lainnya menurun. Perubahan di dalam profil TAG menyebabkan perubahan ke atas sifat-sifat fizikal terutamanya kandungan lemak pepejal adunan duaan minyak. Kandungan lemak pepejal bagi adunan-adunan yang terinterester menurun selepas CIE1 dan meningkat selepas CIE2, kecuali bagi adunan 10:0, 8:2, 7:3, 5:5 dan 9:1 yang menurun selepas CIE1 dan CIE2. Keseluruhannya, CIE1 dan CIE2 berjaya mengubah ciri-ciri fiziko-kimia adunan minyak.

Kata kunci: minyak sawit, minyak bunga matahari, adunan, kandungan lemak pepejal

Introduction

Most native vegetable oils have specific characteristic in their original forms due to their specific chemical composition that reflect specific physical properties and nutritional value, which limit their applications. To enlarge the usage of these oils, they have been modified either chemically (interesterfication or hydrogenation) or physically (fractionation) [1].

Chemical interesterification is an important process for the oils and fats industry. This reaction modifies physical properties of oils by rearrange the distribution of fatty acids on the glycerol backbone without changing their chemical composition [2]. On the other words, the process induces changing on TAG composition. The modified TAG will clearly reflect on solid fat content, which is every type of TAG have their own physical properties like melting point and crystallization.

The objective of this study was to investigate a correlation of simple and chemically interesterified blends containing RBDPO and SFO in TAG composition and solid fat content.

Materials and Methods

Source materials

Refined – deodorized - bleached palm oil (RBDPO) was obtained from Intercontiremtd Specialty Fats Sdn. Bhd. Sunflower oil (SFO)was purchased from a local grocery store (Sunbeam brand) and used without further treatment. All solvents and chemicals used were of analytical grade.

Blend Preparation

RBDPO and SFO were mixed in proportions ranging from 100% RBDPO to 100% SFO in 10% increments (w/w). Nine blend samples with different ratios were prepared [90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90], identified by the mass ratio of RBDPO to SFO.

Chemical Interesterification

Portions (250 g) of the blends, RBDPO and SFO were dried at temperature of 110 ^{o}C for 30 minutes, followed by thorough nitrogen flush to remove moisture and air. Then, the blends were mixed with 0.2% (w/w) sodium methoxide. The interesterification reaction was performed at 110^{o}C (CIE1) and 80^{o}C (CIE2) in a stoppered flask using water bath with constant agitation for one hour. To terminate the reaction, flasks were cooled to below than 60 ^{o}C, followed by addition of citric acid solution (20%) to neutralize the catalyst. The citric acid and sodium methoxide were removed with hot distilled water (3 x 150 mL). Water residual was removed with excess anhydrous sodium sulfate, followed by filtration through a Whatman no. 2 filter. Non-interesterified is abbreviated as DB (direct blending) while chemically interesterified known as CIE.

Pulsed Nuclear Magnetic Resonance (pNMR)

Solid fat content (SFC) was measured by pNMR using Bruker NMR/ND 1844 (Bruker, Germany). This method consists of heating the samples to 70 ^{o}C for 30 minutes and then cooling down to 0 ^{o}C for 90 minutes. The samples were conditioned for 30 minutes at the chosen measurement temperature. During this study, the samples were evaluated at (0, 15, 20, 25, 30, 35 and 40) ^{o}C.

High-Performance Liquid Chromatography (HPLC)

Triacylglycerol composition was determined by HPLC using Waters 1515 Isocratic HPLC Pump, Waters 2414 refractive index (RI) detector. The column used was a Nova-Pak C_{18} (250 mm x 4.6 mm) Waters packed with a particle size of 5 μm. The mobile phase was a mixture of acetone/acetonitrile (63.5:36.5) and the flow rate was 1 mL/min. Triacylglycerol peaks were identified based on the retention time of TAG standards and results ofNoor Lida et al. (2001), Tan & Che Man (2000), Zainal & Yusoff (1999) and Lai et al. (1998) [3-6].

Gas Chromatography (GC)

GC determines fatty acid compositions. The blends were esterified into fatty acid methyl ester (FAME). About 1 μL of the FAME was injected into a Shimadzu (model GC-17A), equipped with a flame-ionization detector (FID), fitted with a polar capillary column BPX70 (0.25 mm internal diameter x 30 cm length x 0.25 μm film thickness). The detector and injector port temperatures were 240 ^{o}C. Carrier gas was nitrogen at 0.3 mL/min. The column temperature was isothermal at 180 ^{o}C.

Results and Discussion

Fatty Acid Composition (FAC)

Table 1 and Figure 1 show fatty acid compositions of RBDPO, SFO and their blends. RBDPO and their blends containing high proportion of RBDPO were characterized by higher content of palmitic and oleic acids. This is because palmitic and oleic are the major fatty acids in RBDPO. While, SFO and blends with high portion of SFO showed a higher content of linoleic acid as the major fatty acid in SFO. The fatty acid compositions of the interesterified blends are not shown as CIE neither affects the degree of saturation nor causes isomerization of fatty acid double bond. Thus, it does not change the fatty acid profile of the starting material [7-9].

Triacylglycerol Composition

Triacylglycerol (TAG) composition of RBDPO and SFO before and after CIE is shown in Figure 2 and 3. The main TAGs in RBDPO were PPO (30.76%), POO (24.09%), POL/SLL (9.46%), PPL (7.97%), PPP (5.87%), POS (5.31%) and OOO (4.19%) (P, palmitic; S, stearic; O, oleic and L, linoleic). The major TAGs of SFO were LLL (28.03%), OLL (27.19%), POL/SLL (11.27%), OOL (10.74%) and PLL (10.05%). Generally, CIE induced only small changes in the TAG composition of RBDPO and SFO.

Table 1. Fatty compositions of RBD palm oil, sunflower oil and their blends in various ratios

RBDPO:SFO ratios	**FAC (wt. %)**						
	C 12:0	C 14:0	**C 16:0**	**C 18:0**	**C 18:1**	**C 18:2**	**C 18:3**
ADB [10:0]	0.289	1.045	44.803	4.042	40.224	8.816	0.152
BDB [9:1]	0.251	0.956	41.561	3.988	38.741	13.605	0.141
CDB [8:2]	0.243	0.906	38.868	3.787	36.614	18.500	0.141
DDB [7:3]	0.252	0.900	36.304	3.627	34.479	23.154	0.126
EDB [6:4]	0.182	0.690	30.744	3.765	34.290	29.141	0.168
FDB [5:5]	0.148	0.561	25.866	3.796	33.220	35.440	0.156
GDB [4:6]	0.123	0.462	21.921	3.735	31.524	41.293	0.154
HDB [3:7]	0.096	0.358	17.978	3.666	29.996	46.416	0.180
IDB [2:8]	0.070	0.267	14.033	3.606	28.878	52.582	0.166
JDB [1:9]	0.046	0.170	10.075	3.538	26.797	58.287	0.174
KDB [0:10]	-	0.068	6.126	3.411	24.863	63.186	0.082

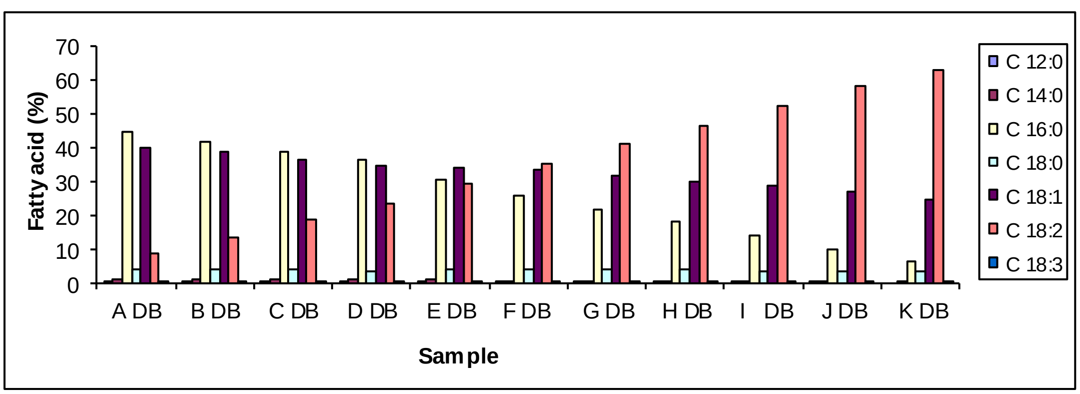

Figure 1. Fatty acid compositions of RBDPO, SFO and their blends in various ratios

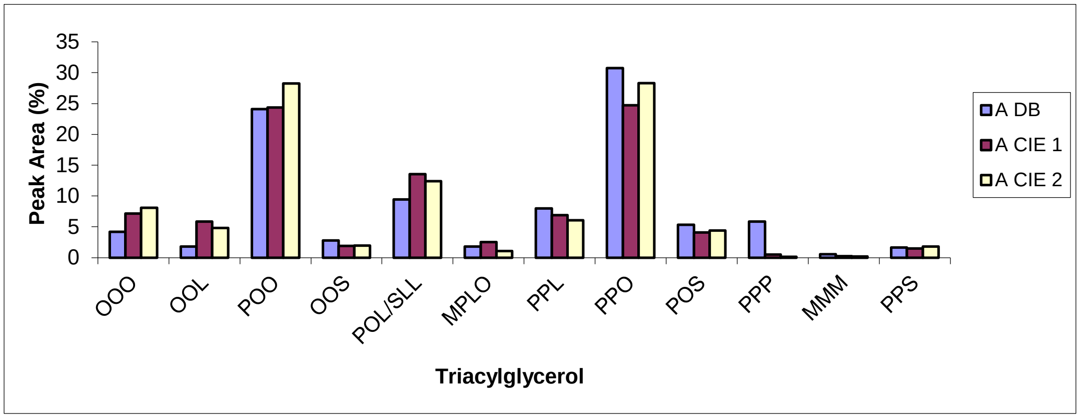

Figure 2. Triacylglycerol compositions of RBDPO before and after interesterification

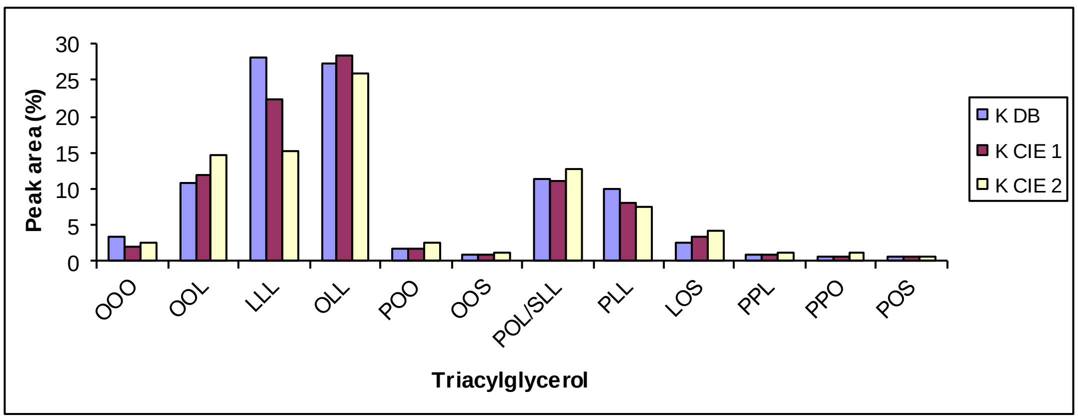

Figure 3. Triacylglycerol compositions of SFO before and after interesterification

Figure 4 shows the TAG composition of some of the binary blends before and after interesterfication of RBDPO/SFO in various ratios. TAG composition of the simple blends of RBDPO/SFO represents a linear combination of the oil component in the blends. For example, as the proportion of SFO increases in the blends, so does the proportion of OOL, LLL, OLL, PLL and LOS. CIE induced enormous changes in the TAG composition of the some samples (G, H and J), but induced a little change for the rest of the samples.

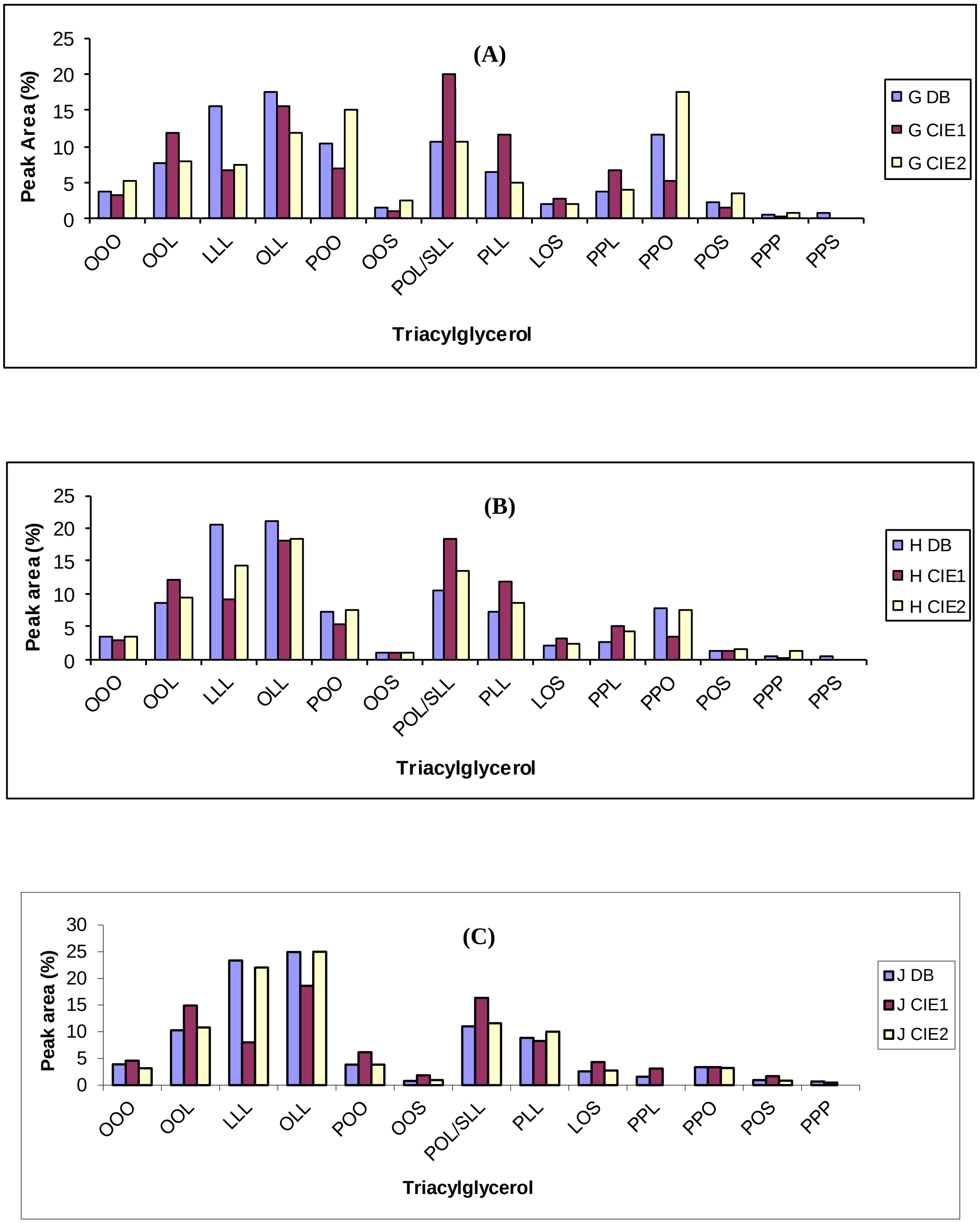

Figure 4. Triacylglycerol compositions of binary blends of RBDPO/SFO before and after interesterification: (A) sample G, (B) sample H and (C) sample J

For example, the proportions of the main TAGs in the sample G DB (containing 40% of RBDPO and 60% of SFO), i.e. the POL/SLL and PLL had increased in CIE1 (86.58% and 81.55% respectively), but decreased in CIE2 (1.03% and 23.47% respectively). CIE1 and CIE2 had resulted increasing in PPL (84.8% and 12.15% respectively) and

OOL (51.99% and 1.67% respectively). However, LLL and OLL had dropped as much as 57.00% and 11.49% respectively in CIE1, and 53.29% and 31.44% respectively in CIE2. PPO, POO and OOO had decreased in CIE1 (55.00%, 33.49% and 12.30% respectively), but increased in CIE2 (51.00%, 44.78% and 37.70% respectively).

Generally, the TAG profiles of the interesterified blends show relative concentrations of several TAGs increased, others decreased, and several new TAGs might also have been synthesized.

Solid fat content (SFC)
The SFC profiles of the simple blend and chemically interesterified RBDPO and their blends in various ratios are shown in Figure 5. The SFC profiles of each sample were significantly changed. The rate of SFC evaluation was dependent on both temperature and proportion of oil in the blends. RBDPO was the hardest fat with 3.12% of SFC at 40 °C. This was due to the high proportion of saturated TAG with respect to the content of palmitic acid as describe in Table 1 compared to SFO. Enormous changes can be seen at temperature from 20 °C to 40 °C, and 5 °C increasing induced dropping more than 40% of SFC. Thus, a little change in temperature induced enormous changes in SFC profile.

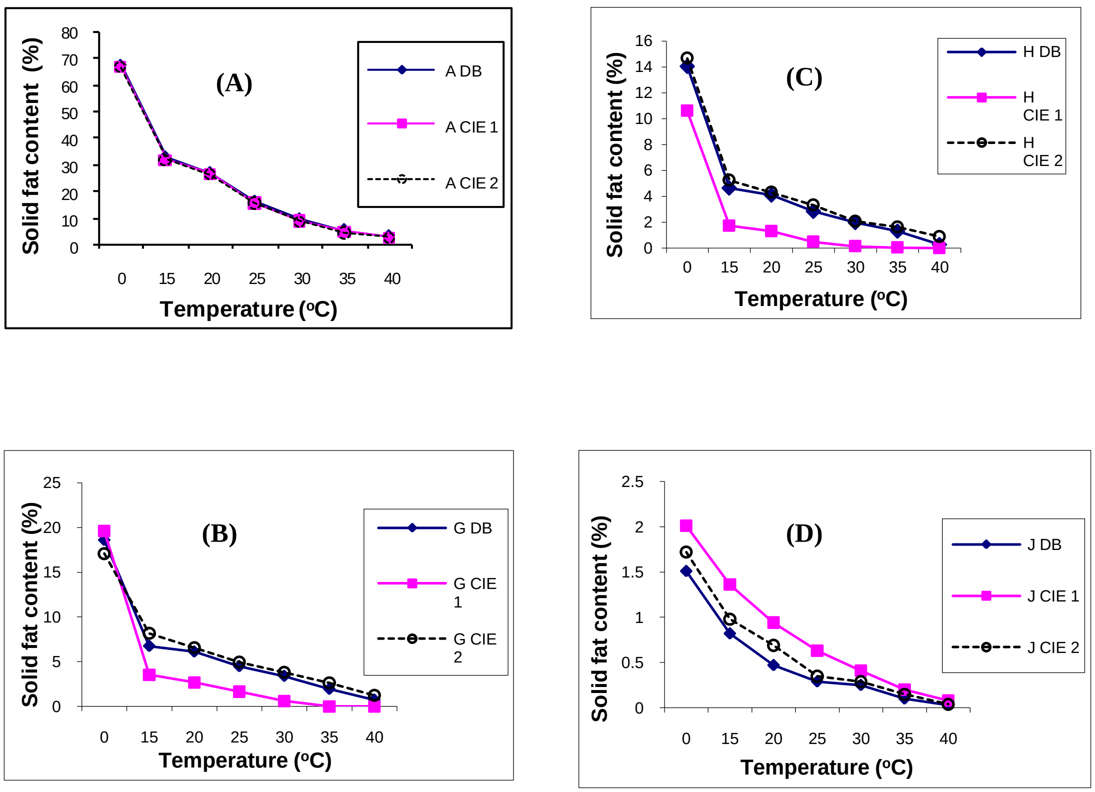

Figure 5. Solid fat content profiles: (A) sample A, (B) sample G, (C) sample H and (D) sample J

SFO is rich in linoleic acid which has very low of melting point. At 15 °C, SFC value of SFO was 0%. Depending on Noor Lida (2001)[3], SFO was fully liquid at temperatures as low as 5 °C, as it was in polyunsaturated fatty acids.

Any changing on TAG composition of the interesterified blends effect the SFC profile. However, TAG composition of RBDPO and SFO after CIE was not much seen. As a result, there was also not much change in their SFC profiles. However, interesterified blends showed various SFC profile due to various type of TAG formed. Enormous changing can be seen in sample G, H and J. For example, sample G DB showed SFC profile higher than sample G CIE1, but lower than G CIE2. Increasing in OOL, POL/SLL and PLL, and decreasing in PPO, POS and PPP for sample G CIE1 alter this result. However, sample G CIE2 decreased in LLL, OLL, POL/SLL and PLL, but increased in PPO, POS and PPP.

SFC profiles of sample H DB was higher than sample H CIE1, but lower than H CIE2. This situation resulted by increasing of OOL, POL/SLL, PLL and LOS, and decreasing of PPO, POS and PPP in sample H CIE1. However, sample H CIE2 has decreased in LLL and OLL, but increased in PPL, PPO, POS and PPP.

SFC profiles of sample J DB was lower than interesterified blends (J CIE1 and J CIE2). It was due to enormous reduction in triunsaturated TAGs (LLL and OLL), but increasing in PPL, LOS and POS for J CIE1. While, sample J CIE2 has decreased in LLL, OOO and OLL.

Conclusion

This study showed that different temperature of interesterification process will produce different interesterified blends. The properties of the interesterified blends cannot be predicted due to randomization of the chemical interesterification. However, SFC profile has direct correlation to TAG composition of the interesterified blends.

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References

1. Basiron, Y., Jalani, B. S. & Chan, K. W. (2000). Advances in Oil Palm Research. Malaysia Palm Oil Board: Malaysia.
2. Petrauskaite, V., De Greyt, W., Kellens, M. & Huyghebaert, A. (1998). Physical and Chemical Properties of Trans-Free Fats Produced by Chemical Interesterification of Vegetable Oil Blends. *Journal of the American Oil Chemists Society*, *75*, 489-493.
3. Noor Lida, H. M. D., Siew, W. L., Chong, C. L. & Kalyana, S. (2001). Characteristics of Simple and Chemically Interesterified Blends Containing Palm Stearin, Sunflower Oil and Palm Kernel Olein and Their Potential Application of The Blends in Fats Spread Formulation. *Oil Palm Bulletin*, *43*, 38-49.
4. Zainal, Z. & Yusoff, M. S. A. (1999). Enzymatic Interesterification of Palm Stearin and Palm Kernel Olein. *Journal of the American Oil Chemists Society*, *76*, 1003-1008.
5. Tan, C. P. & Man, Y. B. C. (2000). Differential Scanning Calorimetric Analysis of Edible Oils: Comparison of Thermal Properties and Chemical Composition. *Journal of the American Oil Chemists Society*, *77*, 143-155.
6. Lai, O. M., Ghazali, H. M. & Chong, C. L. (1998). Physical Properties of Pseudomonas and Rhizomucor Miehei Lipase-Catalyzed Transesterified Blends of Palm Stearin Palm Kernel Olein. *Journal of the American Oil Chemists Society*, *75*, 953-959.
7. Allen, D. A. (1996). Interesterification - A Vital Tool for The Future? *Lipid Technology*, 11-15.
8. Haumann, B. F. (1994). Tools: Hydrogenation and interesterification. *INFORM, 5,* 668-678.
9. Rozendaal, B. F. (1994). Interesterification of Oil and Fats. In *Edible fats and oil: Basic principle and modern practice*, pp. 152-157.