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HUNGARIAN JOURNAL OF INDUSTRY AND CHEMISTRY
Vol. 46(2) pp. 33–36 (2018)
hjic.mk.uni-pannon.hu
DOI: 10.1515/hjic-2018-0015

HUNGARIAN JOURNAL OF INDUSTRY AND CHEMISTRY
HJIC

COMPARISON BETWEEN STATIC AND DYNAMIC ANALYSES OF THE SOLID FAT CONTENT OF COCONUT OIL

VINOD DHAYGUDE *[1], ANITA SOÓS[1], ILDIKÓ ZEKE[2], AND LÁSZLÓ SOMOGYI[1]

[1]Department of Grain and Industrial Plant Technology, Szent István University, Villányi út 29–43, Budapest, 1118, HUNGARY
[2]Department of Refrigeration and Livestock Products Technology, Szent István University, Ménesi út 43-45, Budapest, 1118, HUNGARY

The objective of this work was to compare the physical and thermal characteristics of two coconut oils and their blends which were observed by the results of differential scanning calorimetry (DSC) and pulsed nuclear magnetic resonance (pNMR). Fat blends composed of different ratios (fully hydrogenated coconut oil / non-hydrogenated coconut oil: 25/75, 50/50 and 75/25) were prepared and examined for solid fat content. The solid fat content of samples was determined as a function of temperature by pNMR. The DSC technique determines the solid fat index by measuring the heat of fusion successively at different temperatures. DSC calculates the actual content of solids in fat samples and how it changes throughout the duration of heating or cooling. A characteristic curve is constructed by the correlation of enthalpies. Based on our results, it is clear that both DSC and pNMR techniques provide very practical and useful information on the solid fat content of fats. DSC is dynamic and pNMR is static. A difference in the values of the solid fat indexes of samples was observed which may be due to a fundamental difference between the two techniques. These data can be used by food manufacturers to optimize processing conditions for modified coconut oil and food products fortified with coconut oil.

Keywords: solid fat content, solid fat index, pNMR, DSC, and Coconut oil

1. Introduction

Nowadays, a proper understanding of the crystallization and melting properties of coconut oil systems is essential to increase the number of applications in the food industry. Coconut oil is considered as a multi-component mixture of various triglycerides which determines the physical properties that affect the structure, stability, flavor as well as sensory and visual characteristics of foods [1]. Modification of the properties of solid fat has received much attention in research recently because of its importance during the processing and production of new food products. The crystallization and melting properties of modified fat used as a shortening in bakery products are critical [2]. The crystal networks present in modified fat strongly enhance its texture, stability and acceptance of fatty-food products.

An essential aspect of the industrial manufacture of edible oils and fats is the ability to measure the physical and thermal properties of the materials such as melting and crystallisation profiles, solid fat content (SFC), solid fat index (SFI) and enthalpy. Nuclear magnetic resonance (NMR) spectroscopy and differential scanning calorimetry (DSC) are easier to implement and faster techniques than dilatometry which is time-consuming and inaccurate [3]. NMR has been widely used for the analysis of food materials such as dairy products, fats and oils, in addition to wine and beverages. Over the past two decades, DSC has been increasingly utilised for the thermodynamic characterisation of edible oils and fats as well as the SFI determination of food fats.

Considering the significant scientific and practical importance of the physical properties of coconut oil from a few studies, the solid fat content determined by NMR and DSC methods was investigated and the obtained results compared. Ultimately, this research study is beneficial to the food industry which continues to reformulate many products.

2. Experimental

2.1 Materials

In this research study, Barco coconut oil was used as a source of non-hydrogenated coconut oil (NHCO) which was kindly provided by Mayer's Kft. in Budapest. The fully hydrogenated coconut oil (FHCO) was obtained from local industry in Hungary. Blends of NHCO and FHCO were mixed in 25:75, 50:50 and 75:25 (w/w) proportions. The blends were melted and maintained at 80 °C for 30 mins to erase crystal memory. Subsequently,

*Correspondence: vinod.dhaygude05@gmail.com

Table 1: Fatty acid composition (%) of NHCO, FHCO and their blends.

Fatty acid (%)	FHCO	FHCO:NHCO			NHCO
		75:25	50:5	25:75	
C6:0	0.1	0.225	0.35	0.475	0.6
C8:0	1.9	3.175	4.45	5.725	7
C10:0	2.7	3.4	4.1	4.8	5.5
C12:0	53.3	51.425	49.55	47.675	45.8
C12:1	0.1	0.075	0.05	0.025	–
C14:0	21.3	20.675	20.05	19.425	18.8
C16:0	10	10.025	10.05	10.075	10.1
C18:0	10	8.25	6.5	4.75	3
C18:1 trans	0.03	0.0575	0.085	0.1125	0.14
C18:1 cis	0.3	2.0	3.7	5.4	7.1
C18:2 trans	–	0.02	0.05	0.08	0.11
C18:2 cis	0.1	0.5	0.9	1.3	1.7
C20	0.1	0.1	0.1	0.1	0.1
Other	0.02	0.03	0.05	0.065	0.08

all blends and pure samples of fat were stored in a refrigerator at 10 °C until use.

2.2 Methodologies

Static analysis The static analysis of the solid fat content was conducted by pulsed nuclear magnetic resonance (pNMR) apparatus (Bruker Minispec 300, Bruker GmbH, Germany) according to the official method Cd 16b-93 of the American Oil Chemists' Society (AOCS) [4]. The solid fat content was measured at 5 °C, 10 °C, 15 °C, 20 °C, 25 °C and 30 °C. Three parallel measurements were conducted and average values reported (Fig. 1). Additionally, these SFC values were converted into percentages where the initial value was considered to be 100 %. These percentage SFCs were compared with the SFIs.

Dynamic Analysis Dynamic analyses of the samples were studied by DFC according to AOCS official method Cj 1–94 [4]. Samples of nearly 20 mg were loaded onto the middle of the aluminum pans using a small spatula and hermetically sealed by an empty pan that served as a reference. Samples were cooled to 0 °C at a rate of 1 °C min^{-1} and maintained at this temperature for 10 mins. The heating of blends and pure samples of oil was performed until a temperature of 80 °C was achieved at the same rate as for the cooling. The samples were maintained at 80 °C for 30 mins. The cooling process started after this period and the rate of cooling was 1 °C min^{-1} until the temperature reached −20 °C. Before being heated again to ambient temperature, the samples were maintained at this temperature for 10 mins. After that, heating commenced once more at a rate of 5 °C min^{-1} up to 20 °C at which point calorimetric measurements ended. Three parallel measurements were taken and the average thermogram was reported.

The SFI of fat is expressed as a function of temperature. The numbers of solids in the samples of oil in relation to the temperature were estimated on the basis of the calorimetric results. Areas of the thermograms were calculated and correlated with the percentage of solids in the samples.

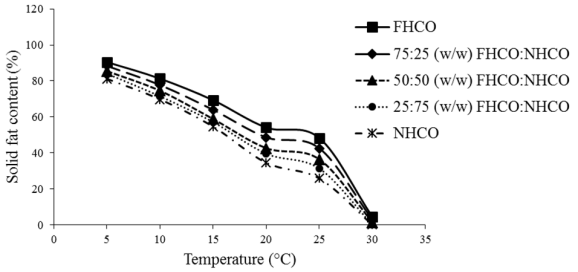

Figure 1: Solid fat content profiles of two coconut oils and their blends.

3. Results and Discussion

3.1 Fatty acid composition

Samples were characterized by their fatty acid composition (see Table 1). The dominant fatty acids in the sample of coconut oil were lauric acid (C12:0) 45.8-53.3 % and myristic acid (C18:0) 18.8-21.3 %. The NHCO exhibited a higher percentage of medium-chain fatty acids and a lower percentage of unsaturated fatty acids. The FHCO was rich in polyunsaturated fatty acids (PUFA) and monounsaturated fatty acids (MUFA).

3.2 Solid fat content according to NMR

The composition of fatty acids and triacylglycerols (TAG) would contribute to the percentage of solid fat particles in liquid oil at various temperatures. The SFC profiles of the original fats and their blends at temperatures ranging from 5 °C to 30 °C are presented in Fig. 1.

The SFC profile of NHCO exhibited low values of 81.06 %, 69.70 %, 54.61 %, 34.54 %, 25.86 % and 0.17 % over the temperature range of 5 °C – 30 °C because of the concentration of fatty acids. In the case of FHCO, the solid fat content was high at 90.49 %, 81.28 %, 69.29 %, 54.15 %, 48.30 % and 4.46 % over the same temperature range. The SFC profiles of blends changed following the addition of FHCO to NHCO. An increase in the maximum values of SFC was also observed by Ribeiro et al. following the addition of fully hydrogenated soybean oil to soybean oil [5]. This can be explained by the changes in the composition of triacylglycerols of the blends. At 5 °C, the blends exhibited SFCs ranging from 84.94 % to 90.02 %, which decreased non-linearly until melting completely at 30 °C. During the blending, the concentration of TAGs with high melting points increased and subsequently the SFC values of blends were modified. In all blends, the SFC values at 30 °C were almost identical to the SFC of the FHCO.

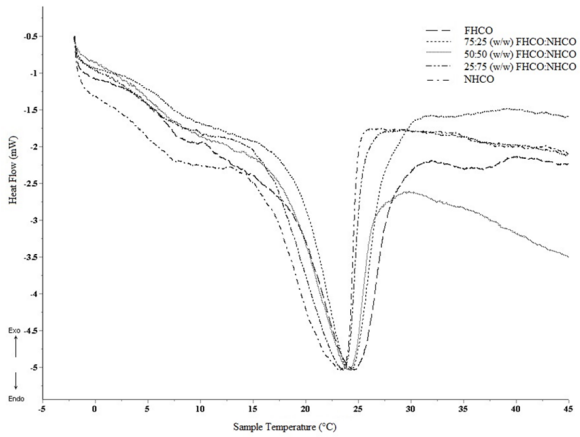

Figure 2: Melting profiles of two coconut oils and their blends.

Table 2: Thermal properties of NHCO, FHCO and their blends.

Sample	Max. temperature (°C)	Peak Enthalpy (J/g)
FHCO	24.61	80.24
75:25(w/w)FHCO:NHCO	24.30	76.21
50:50(w/w)FHCO:NHCO	23.96	63.44
25:75(w/w)FHCO:NHCO	23.52	55.84
NHCO	23.27	46.38

3.3 Melting characteristics

The melting profiles of NHCO in the presence of fully hydrogenated coconut are depicted in Fig. 2. The melting behavior of the original oils and blends was characterized by only one endothermic peak. A similar thermal behavior of coconut oil and hydrogenated coconut oil was observed by one major peak in various studies [6, 7]. Components with the lowest melting points tend to melt first and represent the most unsaturated triglycerides, while components with higher melting points that represent the most saturated triglycerides melt later. Similarly, results showed that NHCO started melting first compared to other samples because of its higher content of unsaturated triglycerides. The addition of FHCO to NHCO did not alter the melting behavior but as the content of FHCO was increased, the peaks according to the melting profiles of blends shifted towards the high-melting temperatures (Fig. 2).

This melting profiles provided an indication of the amount of crystallized fat and the occurrence of polymorphic transitions.

The thermal characteristics of the original oils and their blends are shown in Table 2. No significant differences were observed between the values of onset temperature (T_{on}) and peak temperature (T_p) in addition to the enthalpies of NHCO and FHCO. T_{on} ranged from 15.60 °C to 20.50 °C while T_p ranged from 23.27 °C to 24.61 °C. Melting enthalpies of NHCO following the addition of FHCO increased from 46.38 J/g to 80.24 J/g (see Table 2).

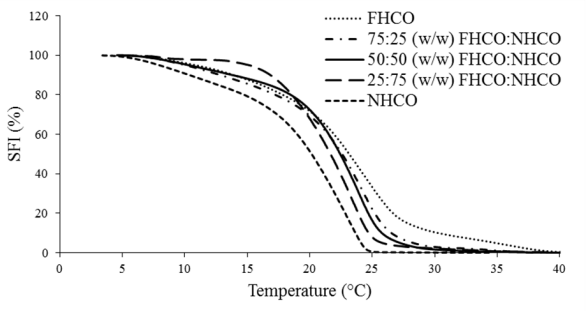

Figure 3: Solid fat index profiles of two coconut oils and their blends.

3.4 Solid fat index (SFI)

The solid-liquid ratio in fats expressed as solid fat content is determined from the melting curves that result from DSC by partial integration. The heat flow into or out of samples of fat was measured as they were heated and cooled isothermally. The estimation of the SFIs of samples is dependent upon the onset and final temperatures of melting. The SFI profiles of all samples calculated by melting thermographs are shown in Fig. 3. Non-hydrogenated coconut oil exhibited a characteristic steep slope and a rapid decrease in the percentage of solids at 20 °C. This ratio of solids to liquids decreases differently in these blends of fat as the temperature rises and is at its minimum for all blends at around 30 °C (see Fig. 3).

4. Discussion

The results obtained from two methods exhibited a wide range of solid fat content values of the same samples. The values of SFC calculated from pNMR results were lower than values of SFI according to DSC where DSC is a dynamic method and NMR is a static method. The values of the percentages of SFC for each blend at 15 °C calculated by DSC were 87.55 %, 88.38 % and 95.95 % (see Fig. 3) but 68.05 %, 68.83 % and 72.35 % when calculated by pNMR, respectively (see Fig. 4). DSC samples exhibited a sharp decline in their SFI or ratio of solids to liquids when heated from 15°C to 25°C, however, the SFC of samples according to NMR exhibited a gradual slope.

DSC measurements of physical behavior were observed under controlled heating conditions. The results of DSC describe the whole melting process whilst being heated. The NMR results indicate the statistical values of solid fat content. The difference between the two measurements was possibly due to the time-dependent process concerning the development of crystal structure where SFI describes the status of the fat system and SFC

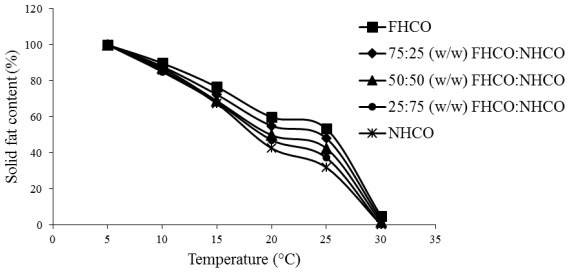

Figure 4: Solid fat content (%) of two coconut oils and their blends.

the solid status after stabilization. In addition NMR identified state vise crystals at respective temperatures. The difference in values may be due to the method of tempering, the rate of heating or cooling, and the degree of accuracy.

5. Conclusion

The results revealed that by combining FHCO with NHCO the melting behavior of blends of coconut oils was modified, leading to significant increments in the melting point and in the maximum solid fat content. These two methods yielded more descriptive and clear information about melting behaviour by determining amounts of solids in the samples of coconut oil in relation to the temperature. Static and dynamic analytical methods showed a difference in the solid-to-liquid ratio of samples which may be due to fundamental differences. The blending of FHCOs with vegetable oils can produce valuable blends of fat of good consistency and with reduced or even in the absence of trans-isomers of unsaturated fatty acids suitable for margarine.

Acknowledgement

This research was supported by the Doctoral School of Food Sciences at Szent István University.

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