

Thermal Properties of the Product of Palm Stearin and Linseed Oil Transesterification

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Abstract: Triacylglycerols are the main constituents of natural fats and oils and contribute directly to their texture and flavor. The DSC (differential scanning calorimetry) of fats and oils is usually performed in order to characterize their melting and crystallization characteristics. The effect of the chemically catalyzed interesterification of two vegetable oils, i.e. palm stearin and linseed oil, on the thermal behavior of the product is studied. The objective of this study is to analyze the impact of the transesterification reaction conditions and of the initial amounts of oils on the thermal behavior of the product. This work shows that both cooling and heating DSC thermograms undergo significant changes as the result of the mixture of linseed oil and palm stearin and of their transesterification.

Key words: Palm stearin, linseed oil, transesterification, DSC, structured lipid.

1. Introduction

Modifying and structuring lipids in the development of innovative food products are increasingly used to enhance their health benefits while satisfying market sensorial demands. Chemical interesterification is one of the main routes for tailoring structured lipids, which are lipids with improved nutritional, physical and sensorial properties. Transesterification is an alternative reaction to hydrogenation, which was often used to modify oils and fats. The hydrogenation changes the vegetable oil into a solid/liquid mixture generating trans fatty acids, for which there are strong evidences to be harmful in the blood [1, 2].

It is well known that melting and crystallization behaviors of edible oils and fats are the most important properties for texture and flavor in many prepared food products. DSC (differential scanning calorimetry) has

been increasingly utilized for thermodynamic characterization of edible oils and fats [3]. These thermal properties are strongly linked to the TAG (triacylglycerol) profile. Modifying the composition of the oils mixtures and the transesterification conditions transforms the DSC profile of the generated edible oil [4].

Linseed oil and palm stearin have been selected because of their properties: they have both unsaturated and saturated chains of fatty acids. Palm stearin contains a higher level of saturated fatty acids whereas linseed oil is known to contain more unsaturated fatty acids. As palm stearin is not an expensive oil, it is convenient to use it to prepare products at low cost with no trans fats. Linseed oil, rich in unsaturated fatty acids, is susceptible to oxidation although it is a major source of omega-3. The increase of linseed oil content in the mixture palm stearin/linseed oil would theoretically produce oil with enhanced value but shorter shelf life.

In this study the correlation of the thermal

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characteristics of the oil products to the chemical composition obtained either by mixing and transesterification is analyzed qualitatively. Theoretical studies that aim to predict quantitatively the thermal behavior for mixing and complete transesterification have been developed in our group either [5].

2. Experimental

2.1 Reagents, Solvents and Standards

Refined palm stearin and linseed oil were obtained from Agro Palma S.A. (Pará, Brazil) and Industrial and Commercial Vegetable Oils Schaeffer Ltd (St. Louis, US) respectively.

2.2 Esterification

Esterification was carried out according to the method used by DE ANGELO [6]. Each oil was melted separately in an oven prior to the esterification in order to obtain a transparent product. The reaction was performed in a 3-neck round-bottom flask with controlled temperature, under vacuum and vigorous agitation. The mixtures were prepared with weight ratios of linseed oil/palm stearin of 100/0, 75/25, 50/50, 25/75 and 0/100 (weight %) and temperatures of esterification were varied from 60-95 °C for 60 min. The catalyst was sodium methoxide at a concentration of 0.4% (w/w). At the end of the esterification, the catalyst was inactivated by the addition of 3 mL of water to the flask. Kieselgur and sodium sulphate were also added to remove the impurities and dry the excess of water respectively. The final product was then submitted to a hot-filtration to remove the humidity, soap and other impurities.

2.3 Purification

Before DSC analysis, the oils were purified to remove impurities thoroughly. The purification method is described as follows: the oil sample (1 g) was mixed with water (4 mL) and chloroform (CHCl₃): methanol (MeOH) (4 mL, 2:1 v/v) and the mixture was vortexed;

the organic phase was removed and kept; more water (4 mL) was then added to the remaining aqueous phase and the mixture was vortexed a second time; the two organic phases were added together and concentrated by rotor-evaporator to give a crude oil.

2.4 Characterization

The open tubular capillary point method was used to determine the melting point of the oils mixtures according to the American Oil Chemists' Society official method [7]. The close tubular capillary point method was used to determine the fusion point of the oils mixtures (American Oil Chemists' Society official method).

DSC analyses were conducted (DSC-60 Shimadzu, Japan) using 5 mg samples, in a closed support, at a 10 °C/min heating rate. The samples were heated to 80 °C at a rate of 10 °C/min and then kept at 80 °C for 5 min. The temperature was then decreased to 80 °C at a rate of 5 °C/min, and this temperature was kept for 15 min. The samples were then reheated to a temperature of 80 °C at a rate of 10 °C/min.

3. Results and Discussion

3.1 Transesterification

There was a change in colour from yellow (beginning) to brown (end of the reaction) when the catalyst was added which strongly showed an evidence of transesterification.

3.2 Melting and Crystallisation Points

The effect of interesterification parameters such as reaction temperatures (from 60-95 °C), reaction time (between 0 min and 60 min) and linseed oil percent on the resulting fusion and melting temperatures was screened on palm stearin/linseed oil mixtures and after reaction. Pure linseed oil has a low fusion temperature of 19 °C because of the presence of linoleic acid whereas palm stearin, with the saturated palmitic acid, has a fusion temperature of 44.5-56.2 °C [8, 9]. Because of their molecular geometries, in comparison

to unsaturated fatty acids, molecules of saturated fatty acids are closer “stacked” together, which increases the oil fusion point. Other parameters such as the size of the chains alter the fusion point: an increase in the size of the chains leads to higher fusion points [10].

The organization of fatty acids in each triacylglycerol molecule affects the final temperatures of fusion and melting. Transesterification yield increases fusion and melting temperatures. At higher reaction temperatures, 80 °C and 95 °C, complete transesterification should be reached fast (20 min) since the transitions have similar values after 20 min and 60 min, except for the fusion point of the mixture with 75% of linseed oil after reaction at 80 °C. From these results, since fusion and melting points after transesterification at 80 and 95° C have similar transitions, there is no need to increase the temperature to 95 °C to conduct the transesterification.

The measurement of fusion and melting temperatures is subject to important random errors because the procedure is prone to some subjective decisions. This can be noted in Table 1, where columns corresponding to 0 min of reaction should be replications but differ as much as 4 °C yet.

4. DSC Analysis

DSC is widely used across a range of applications as has significant advantages compared to the classical thermoanalytical methods, including small sample size (< 20 mg), minimal sample preparation, no use of chemical agents or solvents, short experimental times, and simplicity of operation [11]. These features reduce

the uncertainty in fusion and melting temperatures and allow sensing crystalline transitions.

In order to make comparison easy, the DSC curves are presented in Figs where the ordinates do not share the same origin but share the same unit. Thus, curves are presented in the same figure, stacked one over the other, as for example in Fig. 1.

4.1 Behaviour of Oils during the Heating Process

When heated in a DSC (differential scanning calorimeter), oil samples often exhibit multiple endotherms at temperatures that depend on the composition of the oil used. This is due to the diversity of TAGs (triglycerides) in the oils. Generally, the trisaturated TAGs (SSS) melt at higher temperatures than the triunsaturated TAGs (UUU), whereas the disaturated-monounsaturated (SSU) and monosaturated-diunsaturated (SUU) TAGs melt in between these two extremes [12]. It is also because of the re-crystallization of TAGs crystallites, known as the polymorphism phenomenon, and their subsequent melting.

DSC cooling thermograms obtained for pure palm stearin, pure linseed oil and their transesterified products are shown in Fig. 1. Similarities between these two oils are evident. For palm stearin, in the range of temperatures from -10 °C to 10 °C and 30-50 °C, broad and overlapping transitions are observed due to melting of two or more TAGs complexes. The lower-temperature endotherm is caused by a small amount of olein fraction trapped during the fractionation process, while the more

Table 1 Conditions of transesterification between stearin palm and linseed oil, and fusion and melting temperatures of the products.

Transition	Linseed oil (%)	60 °C			80 °C			95 °C		
		0 min	20 min	60 min	0 min	20 min	60 min	0 min	20 min	60 min
Fusion (°C)	25	49	49	49	50	45	46	49	45	45
	50	49	49	49	47	35	33	46	33	33
	75	42	42	42	42	38	22	42	23	25
Melting (°C)	25	48	48	48	48	35	39	48	39	39
	50	45	45	45	44	28	28	44	29	28
	75	40	40	40	38	24	20	38	21	21

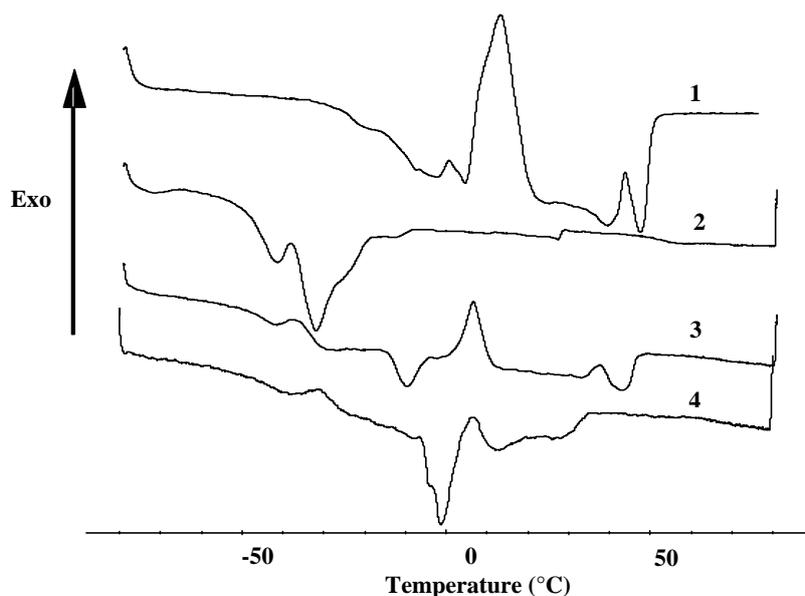


Fig. 1 Differential scanning calorimetry melting curves of oils: (1) palm stearin, (2) linseed oil, (3) physical mixture of palm stearin/linseed oil 50/50, (4) esterified product (conditions: palm stearin/linseed oil 50/50, 95 °C, 60 min, vacuum).

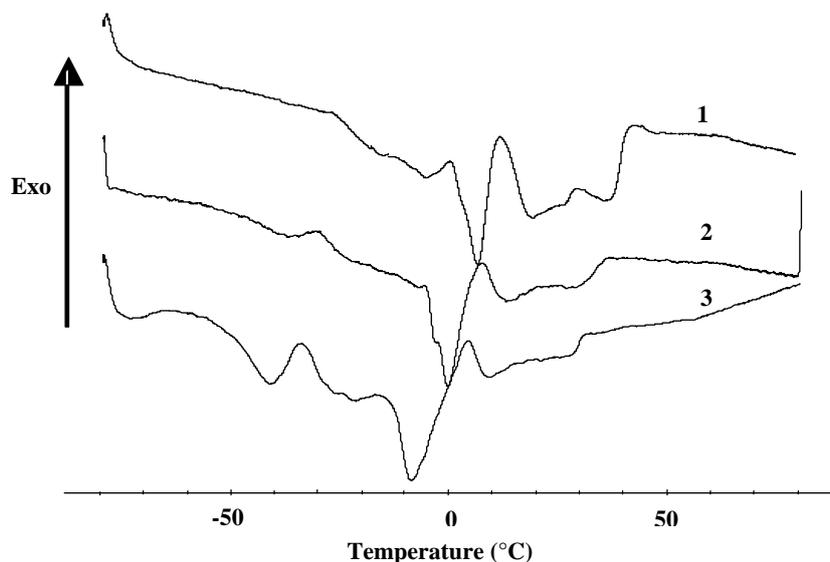


Fig. 2 Differential scanning calorimetry melting curves of stearin palm/linseed oil (esterification conditions: 95 °C, 60 min, vacuum): (1) 75/25, (2) 50/50, (3) 25/75.

prominent higher-temperature endotherm corresponds to the melting of the stearin fraction [13]. The lower-temperature endotherm consists of two or more less-resolved contiguous peaks whereas the higher-temperature endotherm has one main peak with a small leading shoulder peak on the lower temperature side.

The profile of the linseed oil cooling thermogram shows a prominent endotherm at -30 °C (Fig. 1) and a smaller one at -40°C (Fig. 1). This major peak is the

melting peak of the triunsaturated linolenic acid, and the other one that of the triunsaturated linoleic acid.

In addition to the study of the pure oils, the thermal curves of the physical mixture of palm stearin and linseed oil at a ratio of 50/50 were compared to the ones of the esterified product (curve 3, in Fig. 1). The DSC melting curves of the physical mixture exhibits two peaks that correspond to the melting of the stearin fraction at high temperature and of the oleic one at lower temperature. After transesterification, the DSC

melting curve exhibits only one major melting peak (curve 4, Fig. 1) at a temperature in-between the transitions of each of the oils. This is due to the lower concentration of the original TAGs due to chain rearrangements after transesterification.

4.2 Effects of Mixture Composition of Oils

Mixtures of palm stearin/linseed oil 75/25, 50/50 and 25/75 (w/w %) were prepared prior to the reaction of transesterification. Multiple endothermic transitions were detected: a major detected in a (-10 °C; 10 °C) range, and 2 smaller and flatter peaks in the (10 °C; 20 °C) and (30 °C; 40 °C) ranges. An additional endothermic event, peaking at -40 °C has also to be noticed on the DSC thermograms. Addition of linseed oil shifts all the transitions toward lower temperatures. Moreover, the peak present at -40 °C disappears in the mixture with the lowest content of linseed oil (25%). The peak at (-10 °C; -10 °C) shifts to lower temperature and becomes more asymmetric while increasing content of linseed oil. The melting effect of the mixture of oils is not only the attenuation of the

peaks because of the effect of the dilution of the original TAGs, there is also a synergetic effect due to the change in activities [13].

4.3 Effects of Reaction Temperature

Reactions were realized at temperatures ranging from 60 °C to 80 °C and 95 °C. In Fig. 3, it can be seen that as the temperature increases, the melting temperature of the larger endotherm increases. This can be explained by an increase of the randomness of the final rearrangement of the acids on the glycerol backbone when higher reaction temperature is chosen. When the reaction is carried out at 60 °C (curve 3, Fig. 3), small conversion is obtained and the thermogram of the transesterified product is similar to the one of the mixture of palm stearin and linseed oil (curve 3, Fig. 1).

4.4 Effects of Reaction Time on the Cooling Process

When cooled in a DSC, oil samples often exhibit multiple cooling curves that are however, less complex than their respective melting curves. The subdivision of

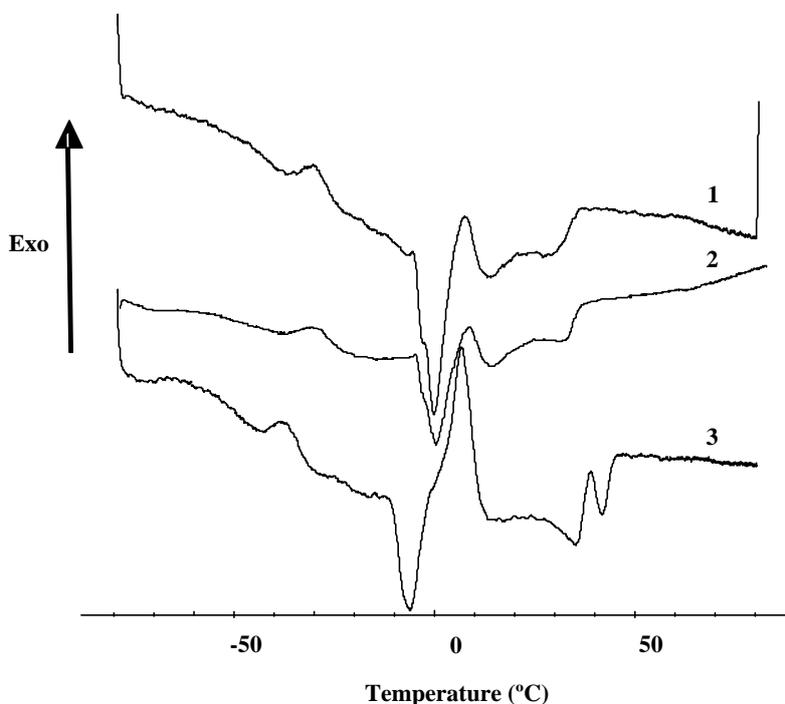


Fig. 3 Differential scanning calorimetry melting curves of stearin palm/linseed oil 50/50 (esterification conditions: 60 min, vacuum) at temperatures of (1) 95 °C, (2) 80 °C, (3) 60 °C.

the crystallisation curve of oil samples into different exothermic regions corresponds to different TAGs types. As the melt is cooled from above the crystallisation temperature of the higher melting TAG component to below its crystallisation temperature, the higher melting component will exhibit a quicker crystallisation and then polymorphism will take place.

Fig. 4 depicts the crystallisation curves for (1) the palm stearin, (2) linseed oil and (3) its mixture. The DSC crystallisation curves of the palm stearin exhibit a minor but broader peak at $-5\text{ }^{\circ}\text{C}$ than the curves of the pure linseed oil and their mixtures. At higher temperatures ($25\text{ }^{\circ}\text{C}$), the exothermic peak, higher in intensity, can be attributed to the crystallisation transition of the stearin fraction (major exotherm) and of small olein fraction content (minor exotherm).

Linseed oil presents small shoulders that can be considered negligible since their intensities are low in the range of ($-50\text{ }^{\circ}\text{C}$; $50\text{ }^{\circ}\text{C}$). Crystallization may not have occurred at the cooling velocity that was programmed ($5\text{ }^{\circ}\text{C}/\text{min}$) because of the low melting temperature of the main TAGs involved.

For the physical mixture and esterified product (curve 3, Fig. 4), the higher temperature exotherm decreases in size which correspond to the behavior of the dilution in a non-crystallizing medium. The transesterification reaction (curve 4, Fig. 4) reduces the amount of purely unsaturated TAGs present in linseed oil and redistributes the unsaturated acids together with the saturated ones present in palm stearin. This broadens the peaks.

4.5 Effects of Mixture Composition of Oils on the Cooling Process

DSC cooling thermograms obtained for esterified palm stearin/linseed oil mixtures are shown in Fig. 5. Lipid crystallisation starts over a range ($10\text{ }^{\circ}\text{C}$; $20\text{ }^{\circ}\text{C}$) that centers at $-5\text{ }^{\circ}\text{C}$. Two well-defined exothermic events appear even at a higher intensity with more palm stearin in the product. Upon the addition of 25% to 75% of linseed oil, there is a shift of $10\text{ }^{\circ}\text{C}$ of the two thermal events and a reduction of the energy required that can be explained by the presence of a dilution effect in a medium that does not crystallize, as is the case of linseed oil because of kinetic constraints.

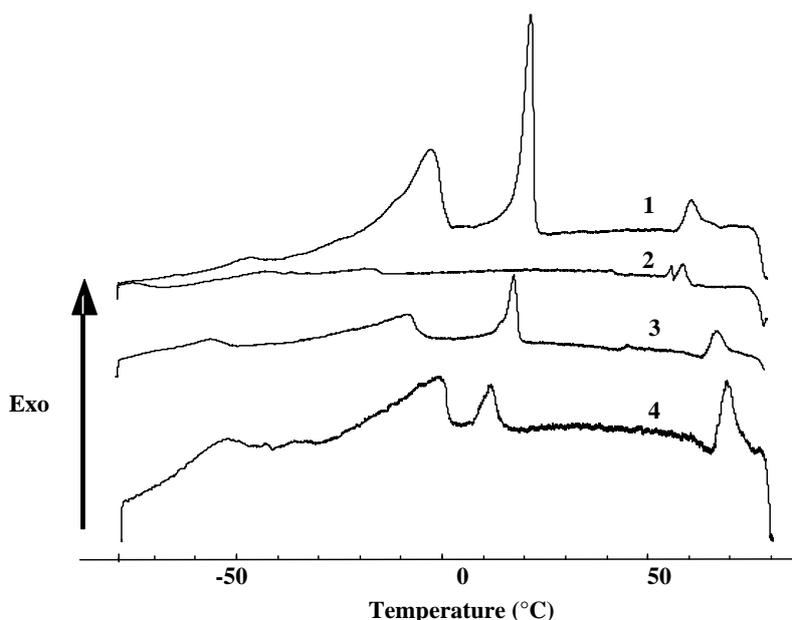


Fig. 4 Differential scanning calorimetry crystallisation curves of oils: (1) palm stearin, (2) linseed oil, (3) physical mixture of palm stearin/linseed oil 50/50, (4) esterified product (conditions: palm stearin/linseed oil 50/50, $95\text{ }^{\circ}\text{C}$, 60 min, vacuum).

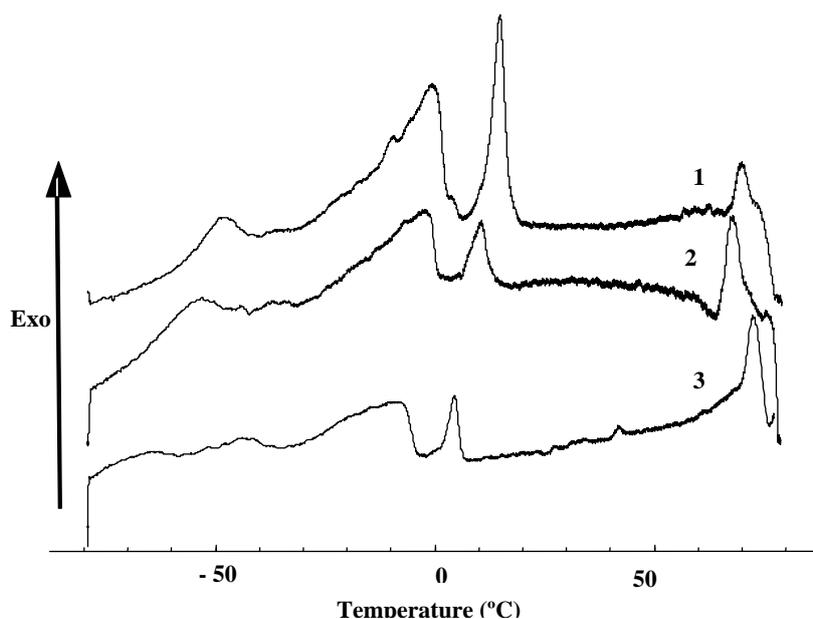


Fig. 5 Differential scanning calorimetry crystallisation curves of stearin palm/linseed oil (esterification conditions: 95 °C, 60 min, vacuum): (1) 75/25, (2) 50/50, (3) 25/75.

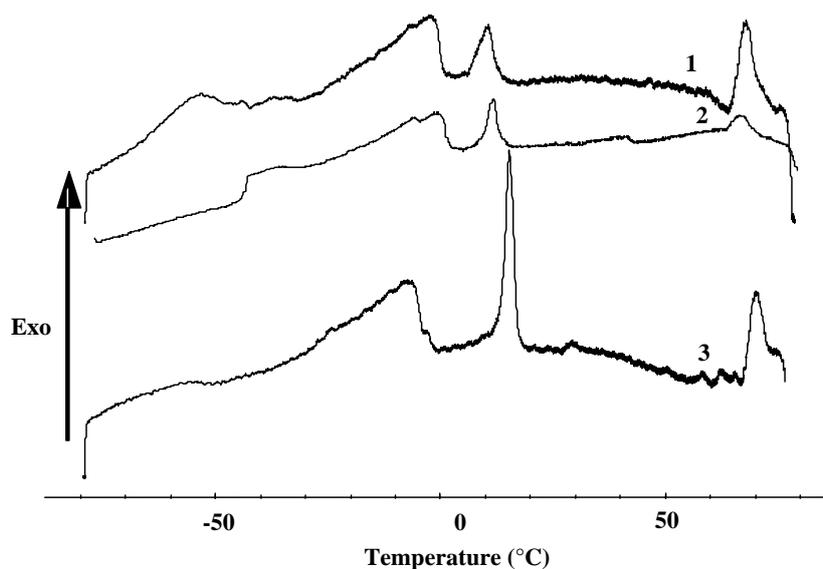


Fig. 6 Differential scanning calorimetry crystallisation curves of stearin palm/linseed oil 50/50 (transesterification conditions: 60 min, vacuum) at temperatures of (1) 95 °C, (2) 80 °C, (3) 60 °C.

4.6 Effects of Reaction Temperature and Time on the Cooling Process

In Fig. 6 the thermograms of transesterification products of a 50/50 mixture of palm stearin/linseed oil are presented. The reactions at 80 °C and 95 °C seem to reach the complete product conversion since there is no obvious change of all the transitions on both chromatograms (curves 1 and 2, Fig. 6). The peaks intensity is decreased and position shifted compared to

the ones at 60 °C because there is a redistribution of the fatty acids over the glycerol backbone more effective at 80 °C and 95 °C leading to lower concentrations of pure TAGs concentrations (Fig. 6).

5. Conclusions

This work showed that both cooling and heating DSC thermograms undergo significant changes as a result of the addition of linseed oil to palm stearin and

of their transesterification. Peaks are shifted and broadened as an effect of the mixture and of the change of the TAGs profile as a consequence of the change of composition because of the rearrangement of fatty acids on the glycerol backbone. Modeling efforts are being undertaken in order to predict the effect of transesterification on these curves that could be useful in order to design new structured lipids. The experimental results presented here are fundamental in order to validate these models.

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References

- [1] Martin, C. A.; Carapelli, R.; Visantainer, J. V.; Matsushita, M.; Souza, N. E. Trans Fatty Acid Content of Brazilian Biscuits. *Food Chemistry* **2005**, *93*(3), 445-448.
- [2] Semma, M. Trans Fatty Acids: Properties, Benefits and Risks. *Journal of health Science* **2002**, *48*(1), 7-13.
- [3] Dollimore, D. Thermal Analysis. *Analytical Chemistry* **1996**, *68*(10), 63R-71R.
- [4] Breitschuh, B.; Windhab, E. J. Direct Measurement of Thermal Fat Crystal Properties for Milk-Fat Fractionation. *Journal of the American Oil Chemists' Society* **1996**, *73*, 1603-1610.
- [5] Santos, M. T.; Le Roux, G. A. C.; Gerbaud, V. Phase Equilibrium and Optimization Tools: Application for Enhanced Structured Lipids for Foods. *Journal of the American Oil Chemists' Society* **2010**, *88*, 223-233.
- [6] Francisco de Angelo, J. Application of The Optimal Experimental Design to the Interesterification Reaction of Palm Stearine with Linseed Oil. Master Thesis, University of São Paulo, 2007.
- [7] American Oil Chemists' Society-AOCS. Official Method Cc 3-25: softening point. USA, 1997c.
- [8] Rittner, H. *Palm Oil: Processing and Use*. (1.ed). Sao Paulo, 1996.
- [9] Gunstone, F. D. Movements toward Tailor-Made Fats. *Progress in Lipid Research* **1998**, *37*(5), 227-305.
- [10] Shahidi, F.; Finley, J. W. *Omega-3 Fatty Acids: Chemistry, Nutrition and Health Effects*; ACS Symposium Series 788, American Chemical Society: Washington, DC, 2001.
- [11] Vittadini, E.; Lee, J. H.; Frega, N. G.; Min, D. B.; Vodovotz, Y. DSC Determination of Thermally Oxidized Olive Oil. *Journal of American Oil Chemists' Society* **2003**, *80*(6), 533-537.
- [12] Tan, C. P.; Che Man, Y. B. Differential Scanning Calorimetric Analysis of Palm Oil, Palm Oil Based Products and Coconut Oil: Effects of Scanning Rate Variation. *Food Chemistry* **2002**, *76*, 89-102.
- [13] Che Man, Y. B.; Haryati, T.; Ghazali, H. M.; Asbi, B. A. Composition and Thermal Profile of Crude Palm Oil and Its Products. *Journal of the American Oil Chemists' Society* **1999**, *76*, 215-220.