



# Thermal properties of palm stearin, canola oil and fully hydrogenated soybean oil blends: Coupling experiments and modeling



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## ABSTRACT

In order to evaluate thermal properties of fats and oils for product design, palm stearin, canola oil and fully hydrogenated soybean oil blends were studied. The fatty acids composition (by gas chromatography), the regiospecific distribution of saturated, monounsaturated and polyunsaturated fatty acids (by Nuclear Magnetic Resonance), the softening point and thermal transitions (by differential scanning calorimetry) were measured experimentally. Iodine value and saponification value were calculated using experimental fatty acids composition. Thermodynamic modeling (Solid-liquid Equilibrium) and computational simulations of solid-liquid transitions were used to predict the Solid Fat Content (SFC) of blends with all possible mass fraction of each oil at 0 °C and 25 °C and to predict changes in heat capacity of the mixtures in the whole melting range. The computational predictions were able to identify the correlation between the amount of saturated fatty acids and melting profile, offering quantitative insights for the whole ternary diagram. The experimental DSC curves, in average, showed more peaks than the predicted curves, due to the use of equilibrium hypothesis by the model and the presence of kinetics factor in experimental DSC.

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## 1. Introduction

The solid-liquid phase behavior of vegetable oils influences many characteristics of fatty foods, including organoleptic properties and flavor release. Chocolate is one of the products largely influenced by this phase behavior. The final melting point of cocoa butter (CB) occurs above typical room temperature but below mouth temperature, making it solid under ambient conditions but melting in the mouth, releasing desired sensory properties, such as cooling sensation (Torbica et al., 2006). However, there are many concerns about CB shortage of supply and increasing prices. Some efforts have been made to overcome that, seeking for CB alternatives (Lipp and Anklam, 1997; Jahurul et al., 2014). A large number of natural and modified fats and oils have been studied to check their suitability to reproduce physical properties close to that of cocoa butter. These studies deal mainly with polymorphism in crystallization (Wille and Lutton, 1966; Bricknell and Hartel, 1998; Loisel et al., 1998; Le Révérend et al., 2010; Miyasaki et al., 2015),

kinetics (Los et al., 2002; Foubert et al., 2002) and physical measurements, such as cloud point, solid fat content, brittleness and hardness (Gregersen et al., 2015). Choose molecules or mixtures components and their ratios in order to match desired properties can be also viewed as a Computational Product Design problem, faced by other areas of study, such as polymers, solvents, fuels and lubricants (Satyanarayana et al., 2009; Chemmangattuvalappil et al., 2009; Yunus et al., 2014; Heintz et al., 2014). However, in order to use these computational approaches to narrow the search space for new mixtures using vegetable oils, it is necessary to be able to compute physical properties in solid-liquid mixtures. The nature of the solid-liquid equilibrium of fats and oils is complex and imposes several challenges to describe in details the multiple solid phases that can be formed (Hjorth et al., 2014; Maximo et al., 2014). In this work we aim to estimate the solid-liquid transitions of fats and oils treating vegetable oils as triacylglycerol mixtures and predicting the distribution of such compounds in solid and liquid phases according to the thermodynamic principle of minimum Gibbs free energy. We have showed how computational tools can be useful to predict SFC of binary blends of vegetable oils, with and without interesterification (Teles dos Santos et al., 2013). This work

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aims to compare computational predictions with experimental data for a system composed by canola oil (CO), palm stearin (PS) and fully hydrogenated soybean oil (FHSO).

## 2. Materials and experimental methods

### 2.1. Materials

Formulations were prepared using palm stearin (PS) from Agropalma (Brazil), fully hydrogenated soybean oil (FHSO) from Cargill (Brazil) and canola oil (CO) from Bunge (Brazil). All reagents used in this study were of analytical grade.

### 2.2. Experimental methods

#### 2.2.1. Blends preparation

Fat blends formulated with CO, PS, and FHSO were prepared at different ratios, according to Table 1. Blends 1–3 represent the original components, blends 4–6 are binary blends, and blends 7–10 are ternary mixtures. The mixtures were prepared after complete melting of the fats at 70 °C, kept under stirring for 10 min to ensure complete homogenization and stored under refrigeration at 5 °C.

#### 2.2.2. Fatty acids composition

Fatty acid (FA) composition was determined on a Varian GC gas chromatograph (430 GC, Varian Chromatograph Systems, USA), equipped with a CP 8412 auto injector. The Galaxie software was used for quantification and identification of peaks. Injections were performed on a 100 m fused silica capillary column (ID = 0.25 mm) coated with 0.2 μm of polyethylene glycol (SP-2560, Supelco, USA) using helium as the carrier gas at an isobaric pressure of 37 psi; linear velocity of 20 cm/s; the makeup gas was helium at 29 mL/min at a split ratio of 1:50; volume injected: 1.0 μL. The injector temperature was set at 250 °C and the detector temperature at 280 °C. The oven temperature was initially held at 140 °C (5 min) and programmed to increase to 240 °C at a rate of 4 °C/min, and then held isothermally for 30 min. Fatty acids (FAs) in the triacylglycerols (TAG) of the blends were converted into fatty acid methyl esters (FAME) by saponification with 0.5 mol/L methanolic sodium hydroxide, followed by refluxing with a solution of ammonium chloride and sulphuric acid in methanol, according to the methodology proposed by Menezes et al. (2013). Qualitative FA composition of the samples was determined by comparing the retention times of the peaks with those of the respective standards of the fatty acids. Quantitative composition was accomplished by area normalization, expressed as mass percent. Samples were run in triplicate and values were averaged.

**Table 1**

Mass fraction of the prepared blends. PS: palm stearin, CO: canola oil, FHSO: fully hydrogenated soybean oil.

Blend	Mass fraction		
	PS	CO	FHSO
1	1	0	0
2	0	1	0
3	0	0	1
4	1/2	1/2	0
5	1/2	0	1/2
6	0	1/2	1/2
7	1/3	1/3	1/3
8	2/3	1/6	1/6
9	1/6	2/3	1/6
10	1/6	1/6	2/3

#### 2.2.3. Regiospecific distribution of fatty acids

The regiospecific distribution of fatty acids on the triacylglycerol backbones was determined by proton-decoupled <sup>13</sup>C NMR (Vlahov, 2008; Standal et al., 2009; Wang et al., 2010). Lipid samples of 250 mg were dissolved in 0.5 mL of deuterated chloroform (CDCl<sub>3</sub>) using 5-mm NMR tubes. NMR spectra were recorded on a Bruker Avance DPX spectrometer operating at 300 MHz. The <sup>13</sup>C spectra were acquired with a spectral width of 2332.090 Hz, pulse of 10.2 μs, and relaxation delay of 30 s. Determination of <sup>13</sup>C was performed at a frequency of 75.8 MHz with a 5 mm multinuclear probe operating at 30 °C. The results show the fatty acids composition in terms of saturated fatty acids, oleic acid (mono-unsaturated) and linoleic + linolenic acids (polyunsaturated). This composition is further depicted in the two possible positions in the glycerol: the middle position (*sn*-2) and the terminal positions (*sn*-1,3), identified by the stereo specific number (*sn*).

#### 2.2.4. Iodine value and saponification value

Iodine values and saponification values were calculated based on the fatty acid composition, according to the AOCS official methods Cd 1c-85 and AOCS Cd 3a-94, respectively (AOCS, 2009).

#### 2.2.5. Softening point

Softening point was determined using the standard open tube melting point method, according to the AOCS official method Cc 3-25 (AOCS, 2009). This analysis was performed in triplicate.

#### 2.2.6. Differential scanning calorimetry (DSC)

The thermal behavior curves were obtained using a differential scanning calorimetry (DSC) cell on a DSC 4000 Perkin Elmer (Perkin Elmer Corp., Norwalk, CT, USA), using nitrogen and sealed aluminum capsules, each containing a sample mass of 5–10 mg. The samples were initially kept at 80 °C for 10 min, then cooled at 10 °C/min up to –60 °C, following an isothermal time of 30 min, and finally heated to 80 °C at 5 °C/min, according to the AOCS Official Method Cj 1–94 (AOCS, 2009). The calibration was performed with indium (temperature of fusion: 156.6 °C and heat of fusion: 28.45 J/g). Curves were processed by Pyris software, and crystallization curves analyzed for the onset of crystallization (*T*<sub>onset</sub> °C), peak crystallization temperatures (*T*<sub>peak</sub> °C) and crystallization enthalpies (Δ*H*<sub>c</sub> J/g).

## 3. Modeling and simulation

### 3.1. Solid-liquid equilibrium modeling

Vegetable oils are formed mainly by triacylglycerols (TAGs), which are molecules formed by three fatty acids sterified to a glycerol structure. Due to their high molecular weight, such compounds tend to crystallize in 3 main polymorphic forms from liquid phase (Sato, 2001). (Fig. 1).

The goal is to estimate, for a given temperature, the amount of TAGs present in the solid and liquid phases. This phase equilibrium problem was solved using the second order condition for phase equilibrium (minimum of Gibbs free energy). This leads to a nonlinear programming problem (NLP) searching for the minimization of the Gibbs free energy function (*G*), subject to linear material balance constraints. The problem can be stated as:

$$\min G(n) = \sum_{i=1}^{nc} \sum_{j=1}^{np} n_i^j \mu_i^j(n) = \sum_{j=1}^{np} n^j g^j \quad (1)$$

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