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Solid Fat Content of vegetable oils and simulation of interesterification reaction: Predictions from thermodynamic approach

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ABSTRACT

The Solid Fat Content (SFC) of vegetable oils is a fundamental property in fatty foods. Also, chemical interesterification (the exchange of fatty acids within and between triacylglycerols) has been used to enhance the melting profile of vegetable oils blends used in food industry. The present work uses a computational approach using Solid–Liquid Equilibrium (SLE) to predict SFC and simulate the chemical interesterification reaction (CI) for different formulations using palm oil (PO), sunflower oil (SFO) and palm kernel oil (PKO). More than 3696 SLE problems are solved, allowing the evaluation of how the fraction of each oil, the temperature and the CI reaction impacts the SFC. The calculated SFC values are compared with experimental data taken from literature. For systems composed of two or one single vegetable oil, the average absolute error (AAE) is 5.2% before CI and 4.2% after CI. For systems composed of three vegetable oils, the AAE is 6.3% before CI and 4.2% after CI. The predictions of SFC before and after CI reaction can aid the food makers to face the combinatorial problem imposed by the choice of the vegetable oil and its fraction in the blend. Future improvements in the pure component properties, thermodynamic model and distribution model of fatty acids in the triacylglycerols can increase the use of computational approaches allowing the experiments to be focused on the most promising formulations in terms of melting profile.

Keywords:
Vegetable oil
Solid Fat Content
Solid–Liquid Equilibrium
Interesterification
Blend

1. Introduction

The Solid Fat Content (SFC) of a vegetable oil blend is responsible for many fundamental characteristics of fatty foods, such as physical appearance, organoleptic properties and spreadability, also influencing plasticity of an edible oil product (Rao et al., 2001). Some attempts to compute SFC and other melting-related properties of vegetable oils (VOs) can be found in the literature. Most of them use non-phenomelogical methods, such as neural networks (Block et al., 1997) and empirical correlations regressing experimental data (Augusto et al., 2012; Fasina et al., 2008; Soares et al., 2009). Thermodynamic approaches are still scarce. The modeling of the Solid–Liquid Equilibrium (SLE) problem in systems composed by fatty acids and triacylglycerols can be found in the works of Boodhoo et al. (2008), Rocha and Guirardello (2009), Wesdorp et al. (2005) and Won (1993). Recently, we have showed how computational tools are useful in predicting SFC of binary blends of VOs, with and without interesterification (Teles dos Santos et al., 2013). The aim of the present work is further compare predicted values of SFC with experimental data and highlight how modeling and simulation can help product design of fatty products matching a desired melting profile.

2. Solid Fat Content

Fig. 1 shows the variables affecting consumers' perception of fat-based foods. It can be noted that many issues contribute to the desired attributes on the final product. The "missing link" corresponds to factors that influence the sensorial perception of food texture (Engelen and Van der Bilt, 2008).

Despite the multiple interactions between these factors, some direct correlations between SFC and desired attributes are established. Some examples gathered from literature are (Arifin et al., 2009; Criado et al., 2008; Lida and Ali, 1998; Osborn and Akoh, 2002; Torbica et al., 2006):

- The SFC between 4 °C and 10 °C determines the ease of spreading of the product at refrigeration temperature and a value not greater than 32% at 10 °C is essential for good spreadability.
- The SFC at 20 °C and 22 °C determines the product's stability and resistance to oil exudation at room temperature.

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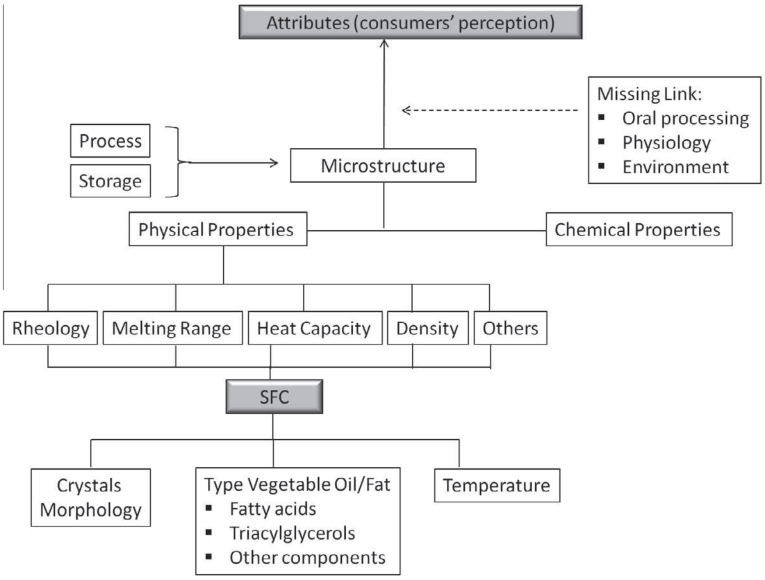

Fig. 1. From fundamental variables to consumers' desired attributes: the role of Solid Fat Content.

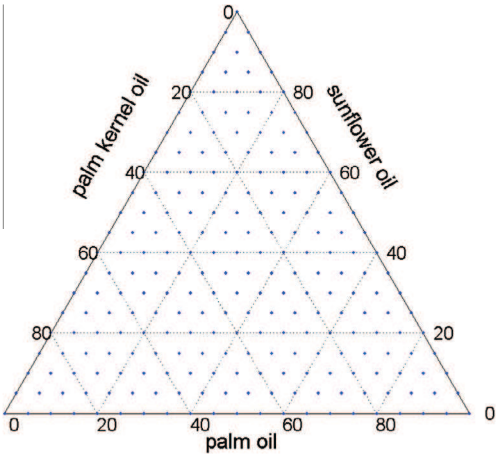

Fig. 2. Ternary diagram with 231 points in which the Solid–liquid Equilibrium problem is solved. Blend PO–SFO–PKO.

- A value of not less than 10% is essential to prevent oiling off.
- The SFC between 35 °C and 37 °C determines the thickness and flavor release.
- Margarines without a waxy mouth feel have a SFC less than 3.5% at 33.3 °C and melt completely at body temperature. A large difference between the SFC at 15 °C and 25 °C is correlated to cooling sensations.
- In baking shortenings, optimal performance is achieved with a SFC between 15% and 25% at the usage temperature whereas an excess of liquid can cause an oiliness sensation decreasing scores of sensorial attributes.
- The temperature range within a fat can retain its consistency is determined by the temperatures within the SFC values lie in the range 15–35%.
- At the range 33–38 °C, the SFC values influence the “mouth feel” or waxy sensations that are induced by the fat.
- The SFC profile of cocoa butter substitutes must have a sharp decrease in solid fat near body temperature as in natural cocoa butter. SFC below 25 °C characterize its hardness, while SFC between 25 °C and 30 °C indicates the

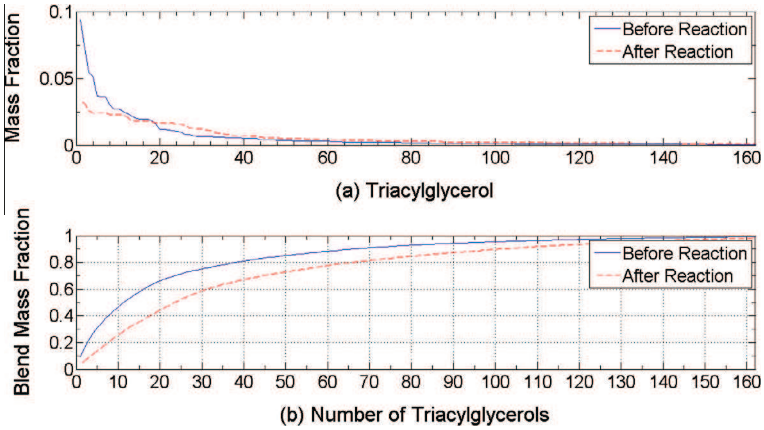

Fig. 3. (a) Calculated mass fraction of each TAG present in the blend PO–SFO–PKO (1–1–1) before and after reaction. (b) Number of TAGs and corresponding mass fraction of the blend PO–SFO–PKO (1–1–1) before and after reaction.

resistance of cocoa butter to heating. In the range of 27 °C to 33 °C, there is a sharp melting of cocoa butter, delivering cooling sensation and flavor release. A high SFC value above 35 °C is related to a waxy taste.

Therefore, direct relationships between desired products attributes and SFC (at specific temperatures) can be established.

3. Interesterification

There are physical (blending and fractionation) and chemical (hydrogenation and interesterification) processes normally used to enhance the use of VOs by changing their composition in terms of triacylglycerols. The demand for more sophisticated fat products increases and the simple physical mixture (*blending*) is not sufficient for matching the desired properties (Dian et al., 2006). The catalytic hydrogenation has the drawback of producing *trans* fatty acids, with negative nutritional effects on consumers' health (Remig et al., 2010). In this scenario, the interesterification emerged as a useful technique to change melting profile of VOs blends. The chemical interesterification (CI) uses catalysts (e.g. metal alcoholate) and heat to promote a random distribution of fatty acids among the three positions of glycerol. On the other hand, enzymatic interesterification uses regioselective lipases that act in the positions 1 and 3 (*sn*-2 position remaining unchanged). Despite the advantages of enzymatic interesterification (milder reaction conditions and regiospecificity), the chemical interesterification has lower catalyst cost, it is easier to scale-up and much faster.

4. Computational approach

4.1. Solid–Liquid Equilibrium modeling

The goal is to predict the solid/liquid ratio given the fraction of each vegetable oil in the blend and the temperature. Computing the phase equilibrium is the solution of a nonlinear programming problem searching for the minimization of the Gibbs free energy function (G), subject to linear material balance constraints. The problem can be stated as:

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

s.t:

$$n_i = \sum_{j=1}^{np} n_i^j \quad i = 1 \ldots nc \qquad (2)$$

$$0 \leqslant n_i^j \leqslant n_i \quad i = 1 \ldots nc; \quad j = 1 \ldots np \qquad (3)$$

where nc and np are the number of different triacylglycerols (TAGs) and the number of phases in the mixture, respectively; n_i^j and μ_i^j represent the number of mols and the chemical potential of TAG i in phase j, respectively and n_i is the total number of mols of TAG i.

Triacylglycerols (TAGs) are the major components of VOs. These molecules crystallize in three main crystalline states: α, β' and β. When a particular polymorphic state is evaluated, another constraint is added: the number of mols of all TAGs in the other two polymorphic states is equal to zero. Then, the optimization algorithm finds the distribution of molecules between the solid and liquid phases that minimizes the Gibbs free energy value. The decision variables are the number of mols of each component i in each phase j (n_i^j).

The intensive Gibbs energy for a phase j (g^j) is the weighted sum of the partial Gibbs energy of all components present in that phase. By definition, the partial Gibbs energy of a component in a mixture

Table 1
Solid Fat Content (calculated and experimental) for different compositions and temperatures before reaction. System PO–SFO–PKO. Single oils and binary blends.

Fraction of each VO	5 °C			10 °C			15 °C			20 °C			25 °C			30 °C			35 °C			40 °C			Average
	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	
Solid Fat Content (%)																									
1–0–0	63.1	42.0	21.1	50.3	39.0	11.3	36.6	33.0	3.6	20.5	22.0	1.5	11.3	11.0	0.3	8.6	10.0	1.4	2.6	7.0	4.4	0.8	1.0	0.2	5.5
3–1–0	43.9	30.0	13.9	34.3	27.0	7.3	24.9	22.0	2.9	13.3	14.0	0.7	7.1	8.0	0.9	5.6	7.0	1.4	1.5	4.0	2.5	0.0	0.0	0.0	3.7
1–1–0	21.6	18.0	3.6	15.1	16.0	0.9	8.9	10.0	1.1	5.2	5.0	0.2	2.7	5.0	2.3	1.7	4.0	2.3	0.0	1.0	1.0	0.0	0.0	0.0	1.4
1–3–0	6.4	8.0	1.6	3.2	6.0	2.8	0.7	3.0	2.3	0.0	2.0	2.0	0.0	2.0	2.0	0.0	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5
0–1–0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0–3–1	8.4	14.0	5.6	2.2	10.0	7.8	0.0	7.0	7.0	0.0	4.0	4.0	0.0	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.2
0–1–1	26.9	27.0	0.1	16.4	22.0	5.6	8.8	17.0	8.2	0.0	12.0	12.0	0.0	7.0	7.0	0.0	2.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	4.4
0–1–3	46.9	45.0	1.9	35.8	33.0	2.8	23.8	25.0	1.2	9.0	19.0	10.0	0.0	14.0	14.0	0.0	7.0	7.0	0.0	1.0	1.0	0.0	0.0	0.0	4.7
0–0–1	70.2	71.0	0.8	60.3	49.0	11.3	44.1	36.0	8.1	23.0	28.0	5.0	3.6	21.0	17.4	0.0	12.0	12.0	0.0	4.0	4.0	0.0	0.0	0.0	7.3
1–0–3	65.6	61.0	4.6	51.6	43.0	8.6	31.8	35.0	3.2	10.7	29.0	18.3	0.0	20.0	20.0	0.0	12.0	12.0	0.0	6.0	6.0	0.0	1.0	1.0	9.2
1–0–1	59.7	56.0	3.7	42.1	44.0	1.9	23.7	37.0	13.3	7.5	31.0	23.5	1.7	22.0	20.3	0.8	14.0	13.2	0.0	9.0	9.0	0.0	3.0	3.0	11.0
3–0–1	58.3	46.0	12.3	39.0	42.0	3.0	22.4	37.0	14.6	10.3	29.0	18.7	6.1	19.0	12.9	4.7	13.0	8.3	0.0	9.0	9.0	0.0	3.0	3.0	10.2
Average			5.8			5.3			5.5			8.0			8.2			5.1			3.1			0.6	

Experimental data: Lida et al. (2002).

is the chemical potential of that component in the mixture (μ_i^j). Therefore:

$$g^j = \sum_{i=1}^{nc} x_i^j(\mu_i^j) => g^j = \sum_{i=1}^{nc} x_i^j(\mu_{i,0}^j + RT\ln\gamma_i^j x_i^j) \tag{4}$$

where γ_i^j and x_i^j are the activity coefficient and molar fraction of component *i* on phase *j*, respectively, and $\mu_{i,0}^j$ is the chemical potential of pure component *i* at the same conditions (*T*,*P*) of the mixture.

For *j* = liquid:

In the reference state of pure liquid, chemical potential is zero. Considering that the liquid phase is ideal, Eq. (4) is simplified to:

$$g^{liquid} = RT\sum_{i=1}^{nc}\left(x_i^{liquid}\ln x_i^{liquid}\right) \tag{5}$$

For *j* = solid:

The chemical potential of a pure component *i* in the solid state *j* in the temperature of the mixture (*T*) is given by (Prausnitz et al., 1999):

$$\mu_{i,0}^{solid(j)} = T\Delta H_{m,i}^{solid(j)}\left(\frac{1}{T_{m,i}^{solid(j)}} - \frac{1}{T}\right) \tag{6}$$

where $\Delta H_{m,i}^{solid(j)}$ and $T_{m,i}^{solid(j)}$ are, respectively, the melting enthalpy and melting temperature of TAG *i* in solid state *j*. Using Eq. (6) on Eq. (4), one have for the solid phases:

$$g^{solid(j)} = Rt\sum_{i=1}^{nc} x_i^{solid(j)}\left(\frac{\Delta H_{m,j}^{solid(j)}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,j}^{solid(j)}}\right) + \text{In}(\gamma_i^{solid(j)} x_i^{solid(j)})\right) \tag{7}$$

4.2. Excess Gibbs energy model

Activity coefficients are needed to compute Gibbs free energy on solid states (Eq. (7)). The definition of activity coefficient is given by:

$$RT\ln\gamma_i(T,P,x) = \bar{g}_i^E = \left(\frac{\partial n g^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{8}$$

So, an Excess Gibbs energy model must be used. The 2-sufixe Margules model was chosen for three main reasons: (1) it is suitable for mixtures where the components have similar molar volume, shape and chemical nature (Prausnitz et al., 1999); (2) an experimental database in TAGs is available allowing to compute the model parameters (Wesdorp et al., 2005) and (3) it allows flexibility/simplicity required in the optimization step. The 2-sufixe Margules equation for multicomponent mixtures is given by:

$$g^E = \sum_{i=1}^{nc}\sum_{j=i+1}^{nc} A_{ij}x_i x_j \tag{9}$$

$$A_{ij} = 2qa_{ij} \tag{10}$$

The parameter q is a measure of molecular size in the considered pair (*i*,*j*) and x_i is the molar fraction of TAG *i*. The parameters a_{ij} are related to interactions between TAGs *i* and *j* (Prausnitz et al., 1999).

The necessary binary interaction parameters (A_{ij}) are calculated using correlations with the isomorphism between the two triacylglycerols *i* and *j* (Wesdorp et al., 2005). Once the activity coefficients are estimated, the Gibbs energy in each phase can be calculated using Eq. (5), (7).

4.3. Melting temperature and melting enthalpy

For each TAG, six values are required: three values of melting enthalpies and three values of melting points (each one corresponding to a solid–liquid transition). A program, developed in FORTRAN 90, includes a set of available experimental data. Due to the high number of TAGs that can be formed from just a few fatty acids, it is frequent that experimental data is not available for a given TAG or not available in all three polymorphic states. In such cases, the predictive methods of Zeberg–Mikkelsen and Stendby (1999) and Wesdorp et al. (2005) are used.

4.4. Solution approach

The optimization step (problem represented by Eqs. (1)–(3)) was implemented in GAMS (v.23) (Rosenthal, 2008) using a solver based on a Generalized Reduced Gradient Method (CONOPT 3). This optimization program was then coupled (using batch files) with the main program written in FORTRAN 90, which handles the calculation of interaction parameters, melting temperature,

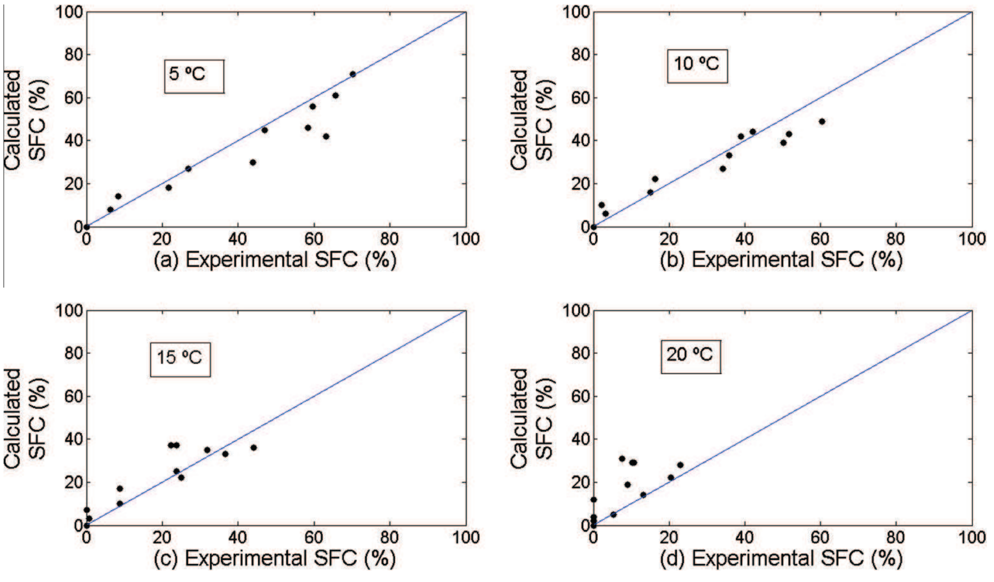

Fig. 4. Calculated vs. experimental Solid Fat Content for binary blends and pure systems composed of PO–SFO–PKO before chemical interesterification reaction.

melting enthalpy and the generation of triacylglycerols from fatty acids data. This last one is done by random distribution of fatty acids in the glycerol, generating all possible TAGs by combinatorial analysis, as described in details in our previous work (Teles dos Santos et al., 2013). The results from the optimization step are the number of mols of each TAG in each phase (solid and liquid). Thus, summing the total number of mols in solid phases, one can compute the SFC given the temperature and fraction of each vegetable oil in the blend.

4.5. Case study

The methodology was applied to a ternary system composed of palm oil (PO)–sunflower oil (SFO)–palmkernel oil (PKO) before and after chemical interesterification. The computational results from the present work were then compared with SFC experimental data from Lida et al. (2002). The experimental data is available in 8 different temperatures and in 16 fractions of each oil in the blend (including pure oils and binary blends). A total of 256 experimental points are available: 128 before CI (16 composition × 8 temperatures) and 128 after CI (16 compositions × 8 temperatures). Among them, 64 refer to ternary blends. In the present computational approach, an increment of 5% in each vegetable oil is used. This allows covering all blends with available experimental data.

Fig. 2 shows all points in a ternary diagram covered by the computational predictions.

According to Fig. 2, for a given temperature, 231 optimization problems must be solved, covering a large set of different fractions of each VO in the blend (57 binary, 3 pure vegetable oil and 171 ternary problems). If one considers that the same diagram is evaluated before and after CI, a total of 462 formulations are covered at a single temperature. Spanning the procedure to only 8 temperatures, 3696 data on SFC can be evaluated. The main program deals with TAGs generation from fatty acid data, activity coefficient and pure component properties estimation; then the optimization step is solved in the GAMS program, giving the ratio solid/liquid. This procedure continues automatically until the whole diagram is covered for a given temperature.

5. Results

5.1. Triacylglycerol composition analysis

Although the work of Lida et al. (2002) has the TAG composition of the mixtures (from HPLC analysis), the authors highlight a set of uncertainties: many TAGs cannot be identified due to the lack of standards and TAGs with equivalent carbon numbers are very similar, thereby making their identification, based on relative retention times, difficult and uncertain. In addition, no experimental composition is given for a system composed of three vegetable oils after CI reaction.

For these reasons, for each point on Fig. 2, the present work uses predicted TAG composition from the known fatty acid data of each vegetable oil (taken from Lida et al. (2002)). This fatty acid composition is: PO (lauric acid: 0.2%, myristic acid: 1.0%, palmitic acid: 42.9%, stearic acid: 4.4%, oleic acid: 40.8%, linoleic acid: 10.2%); SFO (myristic acid: 0.1%, palmitic acid: 6.3%, stearic acid: 3.7%, oleic acid: 24.3%, linoleic acid: 65.1%); PKO (caprylic acid: 4.7%, capric acid: 3.8%, lauric acid: 44.5%, myristic acid: 13.7%, palmitic acid: 8.4%, stearic acid: 2.8%, oleic acid: 18.1%, linoleic acid: 2.9%).

Two TAG compositions must be estimated: the TAG composition of the system resulting from the physical mixture of the oils and the TAG composition of the product of the CI reaction among the oils. In the first case, the TAG composition of each oil is first

Table 2
Solid Fat Content (calculated and experimental) for different compositions and temperatures after reaction. System PO–SFO–PKO. Single oils and binary blends.

Fraction of each VO	5 °C			10 °C			15 °C			20 °C			25 °C			30 °C			35 °C			40 °C			Average
	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	
Solid Fat Content (%)																									
1–0–0	62.2	42.0	20.2	53.9	39.0	14.9	42.5	33.0	9.5	30.2	22.0	8.2	21.3	11.0	10.3	13.8	10.0	3.8	8.3	7.0	1.3	0.8	1.0	0.2	8.6
3–1–0	36.8	20.0	16.8	30.2	17.0	13.2	20.5	12.0	8.5	11.7	5.0	6.7	7.7	5.0	2.7	3.8	4.0	0.2	1.6	1.0	0.6	3.4	0.0	3.4	6.5
1–1–0	19.7	8.0	11.7	13.5	5.0	8.5	5.9	2.0	3.9	2.8	2.0	0.8	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1
1–3–0	3.5	1.0	2.5	0.2	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
0–1–0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0–3–1	2.3	0.0	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
0–1–1	17.3	12.0	5.3	6.2	6.0	0.2	0.5	3.0	2.5	0.0	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1
0–1–3	41.6	32.0	9.6	27.5	22.0	5.5	13.6	14.0	0.4	0.9	11.0	10.1	0.0	6.0	6.0	0.0	2.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	4.2
0–0–1	65.0	75.0	10.0	53.8	51.0	2.8	36.3	36.0	0.3	14.7	28.0	13.3	1.3	13.0	11.7	0.0	13.0	13.0	0.0	4.0	4.0	0.0	0.0	0.0	6.9
1–0–3	59.6	46.0	13.6	48.2	33.0	15.2	32.9	25.0	7.9	17.7	19.0	1.3	5.2	13.0	7.8	0.0	5.0	5.0	0.0	1.0	1.0	0.0	0.0	0.0	6.5
1–0–1	55.0	34.0	21.0	41.2	27.0	14.2	29.4	20.0	9.4	16.4	15.0	1.4	7.7	9.0	1.3	0.8	4.0	3.2	0.0	0.0	0.0	0.0	0.0	0.0	6.3
3–0–1	54.0	33.0	21.0	43.5	28.0	15.5	30.6	21.0	9.6	20.2	15.0	5.2	12.8	10.0	2.8	4.7	5.0	0.3	1.1	1.0	0.1	0.0	0.0	0.0	6.8
Average			11.2			7.5			4.3			4.0			3.6			2.3			0.6			0.3	

Experimental data: Lida et al. (2002).

estimated separately (by computational random distribution of fatty acids in the glycerol); then, a material balance of the TAGs gives the TAG composition of the mixture. In the second case, first a material balance of all fatty acids present in each oil gives the overall fatty acid composition; then, a computational random distribution of these fatty acids in the glycerol is done, resulting in an indirect way to simulate the effect of the chemical interesterification.

As an example, all TAGs generated for the blend PO–SFO–PKO (1–1–1) before (189 TAGs) and after CI (206 TAGs) are given as Supplementary data (TernaryBlend_TAGs.xls).

Fig. 3a shows the mass fraction of each TAG in this ternary blend (1–1–1) before and after CI reaction. The number of TAGs that must be considered to cover a specified total mass fraction of the blend is shown on Fig. 3b.

We observe that the number of TAGs increases after CI reaction. Also, among the theoretical TAGs, many of them can be considered as traces, as they have very low mass fraction. The threshold overall mass fraction of 85% is used, which means that the number of TAGs used in each SLE problem in Fig. 2 is that corresponding to 85% of the mass of the mixture. As discussed in previous work (Teles dos Santos et al., 2013), tests have shown that this value is a good compromise between accuracy in mixture representation, computational time and the uncertainties on pure component properties predictions.

5.2. Pure vegetable oils and binary blends of the system PO–SFO–PKO

5.2.1. Before CI reaction

Table 1 shows the predicted and experimental data before reaction for pure vegetable oils and binary blends.

From Table 1 one can note that:

- The present study was able to identify that in all temperature range, the blend 0–1–0 (pure SFO) is liquid. This is due to the SFO composition: 65.1% in linoleic acid (C18:2) and 24.3% in oleic acid (C18:1), comprising a total of 89.4% on unsaturated fatty acids with low melting points.
- The blend with larger AAE (11%) was the blend 1–0–1 (50% PO–50% PKO). However, we can find points with good agreement between experimental and calculated results for this blend (e.g., at 10 °C, SFC calculated = 44.0%, experimental 42.1%).
- The temperature with higher average absolute error (considering all blends) is 25 °C, with an AAE of 8.2%.

Fig. 4 shows the calculated vs. experimental values of SFC at four different temperatures present on Table 1. The overall average absolute error before CI reaction (all data on Table 1) is 5.2% in SFC.

5.2.2. After CI reaction

Table 2 shows the comparative results for the blends after chemical interesterification reaction.

The following points can be outlined from Table 2:

- Pure SFO (0–1–0) and the blend formed by 75% SFO and 25% PKO (0–3–1) are liquid at all evaluated temperatures (experimental) and the model was able to identify it. The exception is at 5 °C, in which there are still 2.3% in solids (experimental). For this temperature, the model predicts 0% in SFC.
- The larger average absolute error is 8.6% for pure palm oil (1–0–0). Even for this case, points with very high agreement were observed. For example, at 40 °C, SFC calculated = 1%, SFC experimental = 0.8%.
- High agreements were observed for some cases. For example: system (0–0–1) at 15 °C (SFC experimental = 36.3%, SCF calculated = 36.0%); system (0–1–1) at 10 °C, (SFC experimental = 6.2% SCF calculated = 6.0%).
- High deviations are also observed. The larger value is 21% in SFC for the binary blends formed by palm oil and palm kernel oil (1–0–1 and 3–0–1) at 5 °C.

Fig. 5 shows the calculated vs. experimental values of SFC at four different temperatures. The overall average absolute error after CI reaction is 4.2% in SFC.

5.3. Ternary blends of the system PO–SFO–PKO

There are four experimental formulations in which all three vegetable oils are used, resulting in 64 experimental points: 32 before reaction (4 compositions × 8 temperatures) and 32 after reaction (4 compositions × 8 temperatures). Table 3 shows the calculated and experimental results.

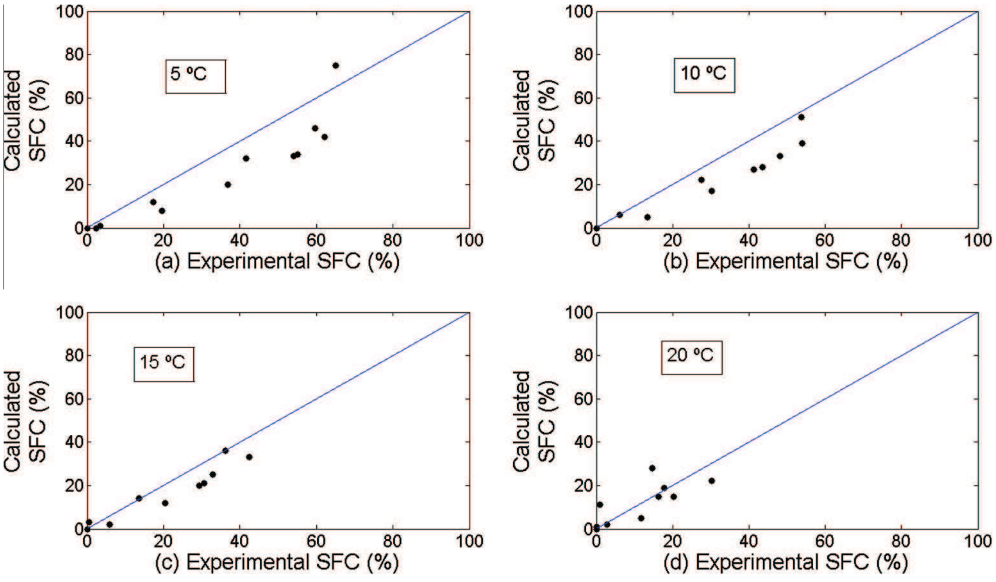

Fig. 5. Calculated vs. experimental Solid Fat Content for binary blends and pure systems composed of PO–SFO–PKO after chemical interesterification reaction.

Table 3
Solid Fat Content (calculated and experimental) for different compositions and temperatures before and after reaction. System PO–SFO–PKO. Ternary blends.

Fraction of each VO	5 °C			10 °C			15 °C			20 °C			25 °C			30 °C			35 °C			40 °C			Average
	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	Exp	Calc	Abs error	
Solid Fat Content – before reaction (%)																									
4–1–1	42.0	36.0	6.0	28.2	32.0	3.8	17.4	27.0	9.6	8.3	20.0	11.7	4.7	12.0	7.3	2.7	10.0	7.3	0.0	6.0	6.0	0.0	2.0	2.0	6.7
1–4–1	9.8	12.0	2.2	1.9	10.0	8.1	0.0	8.0	8.0	0.0	5.0	5.0	0.0	3.0	3.0	0.0	2.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	3.5
1–1–4	51.1	47.0	4.1	37.4	34.0	3.4	20.9	28.0	7.1	5.8	22.0	16.2	0.0	15.0	15.0	0.0	8.0	8.0	0.0	4.0	4.0	0.0	0.0	0.0	7.2
1–1–1	32.5	30.0	2.5	18.4	26.0	7.6	7.2	22.0	14.8	0.0	16.0	16.0	0.0	11.0	11.0	0.0	7.0	7.0	0.0	4.0	4.0	0.0	0.0	0.0	7.9
Average			3.7			5.7			9.9			12.2			9.1			6.1			3.5			0.5	
Solid Fat Content – after reaction (%)																									
4–1–1	44.6	21.0	23.6	33.8	17.0	16.8	22.2	13.0	9.2	12.5	8.0	4.5	7.3	5.0	2.3	3.3	3.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	7.1
1–4–1	7.0	0.0	7.0	1.1	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0
1–1–4	43.8	30.0	13.8	30.8	20.0	10.8	17.7	14.0	3.7	6.5	10.0	3.5	0.0	5.0	5.0	0.0	2.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	4.9
1–1–1	27.9	10.0	17.9	16.0	7.0	9.0	7.5	4.0	3.5	2.5	2.0	0.5	0.0	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0
Average			15.6			9.4			4.1			2.1			2.1			0.6			0.0			0.0	

Experimental data: Lida et al. (2002).

The model was able to identify that in all temperatures the blend with higher content in sunflower oil (1–4–1) is always the one with lowest SFC. Concerning the influence of temperature in the performance of the model, the highest deviation was 12.2% at 20 °C (before reaction) and 15.6% at 5 °C (after reaction). For the not interesterified blends, the highest deviation observed is that of the system 1–1–1 (7.9%). For interesterified blends, the highest deviation (7.1%) is observed in the system with higher amount of palm oil (4–1–1). The overall average absolute deviation is 6.3% before and 4.2% after reaction.

Fig. 6 shows how the fraction of each vegetable oil influences the SFC over the 231 points of Fig. 2. The influence of the CI reaction can be also observed.

The whole diagram before CI reaction is achieved in 1 h 45 min 5 s while after reaction requires 2 h 36 min of computational time (PC Intel(R) Core(TM)2 Quad CPU Q9550 2.83 GHz, 2.00 GB RAM, Windows Vista 32 bits).

It can be noted a sharp reduction in SFC after CI reaction: when the VOs are only mixed, most part of the formulations result in a SFC between 20% and 50% (Fig. 6 left); after CI, most part of the diagram moves towards a SFC between 0% and 25% (Fig. 6 right).

This reduction in SFC is due to the reduction in the content of saturated TAGs (higher melting point) after reaction. This is caused by the redistribution of fatty acids and the consequently formation of a high number of new or unsaturated TAGs with lower melting point, not present in the original blend. The Supplementary data gives an illustrative example, where some saturated TAGs are "diluted" after reaction.

The region with lower SFC or at liquid state is that with higher amount of sunflower oil (SFO). As discussed earlier, this is a highly unsaturated vegetable oil, with 89.4% of low melting unsaturated fatty acids. Also, the region with higher SFC is that in which the SFO fraction tends to zero.

One feature arising from Fig. 6 is that similar reductions in SFC can be accomplished either promoting CI in a given composition or changing the fraction of each oil in the blend.

Some high relative errors can be observed (Table 1–3). For example, for the system 0–3–1 at 10 °C before reaction (Table 1), SFC experimental = 2.2%, SFC calculated = 10.0% (relative error: 354.54%). However, the absolute error is only 7.8% in solids, which can be considered acceptable given that for product formulation there are normally desired ranges, rather than single desired values (as described in Section 2).

For both set of data (before and after reaction), the lowest absolute error occurs at the highest temperature (40 °C). This is due to the identification of a single liquid phase (SFC = 0) in the majority of the blends, i.e., there is a complete fusion at this higher temperature.

The main model limitations concern:

(a) Pure component property predictions (melting point/melting enthalpy) are evaluated for each TAG. Depending on the case, TAGs with less accurate properties can have a large amount in the composition of the mixture, leading to poor predictions on SFC. Uncommon TAGs are also very difficult to get their pure properties.
(b) Deviations of real systems from the simplification hypotheses of random distribution of fatty acids in the glycerol.
(c) Limitations from the Excess Gibbs energy models used (activity coefficients).

6. Conclusions

For the two sets of systems analyzed (pure + binaries blends and ternary blends) the present computational methodology showed similar performance and a slightly superior performance

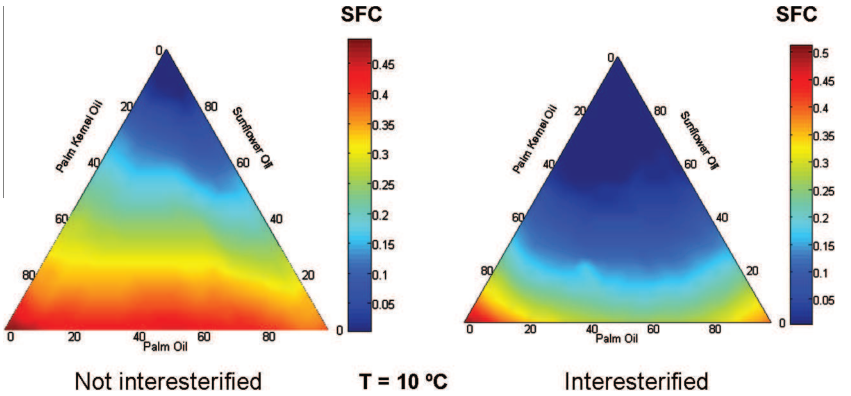

Fig. 6. Theoretical ternary diagrams for the blends composed of PO–SFO–PKO at 10 °C before (left) and after (right) reaction.

for the systems after interesterification. Given the average accuracy of the method and its predictive nature, this computational approach can be useful as a first attempt to cope with the large set of possible formulations and the high number of triacylglycerols present in natural fats and oils. Estimating the SFC value with relative accuracy can be useful to orient experiments, which can offer more accurate analysis in a smaller set of formulations. The present work proposes that the established experimental knowledge, the use of thermodynamic models and computational tools can be integrated in order to make experimental procedures more efficient. The objective is not to obtain detailed description of solid phases for one single mixture but rather be able to explore the combinatorial problem when using different vegetable oils, in different fractions and temperatures.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfoodeng.2013.11.012.

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