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Modeling and simulation of melting curves and chemical interesterification of binary blends of vegetable oils

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H I G H L I G H T S

SFC curves of binary blends of vegetable oils can be predicted.
Chemical interesterification of binary blends of vegetable oils can be simulated.
Minimization of Gibbs energy is useful for predict thermal profile of vegetable oils.
Fat-based product design can take advantage of computational tools in SFC evaluation.

A B S T R A C T

A Solid–Liquid Equilibrium model coupled with an algorithm for direct minimization of the Gibbs free energy function was used to compute the melting profiles for binary blends of vegetable oils. The effect of interesterification on the Solid Fat Content (SFC) is simulated by using a completely random distribution of fatty acids on the glycerol structures. The methodology was applied to different blends of 6 vegetable oils: canola oil, fully hydrogenated palm oil stearin, palm oil stearin, cottonseed oil, milkfat and corn oil. The predicted results were compared with experimental data from literature and the average absolute error in SFC was 3.33% (physical mixture without interesterification) and 4.13% (after interesterification). Additionally, two qualitative aspects also observed in experimental works could be computationally detected: the existence of temperatures in which the blends have the same SFC before and after reaction and the fact that randomized blends tend to melt at lower temperatures than their corresponding mixtures. The results reinforced the potential use of computer-based tools to explore new formulations aiming to match a desired melting range, reducing the experimental efforts in product design where vegetable oils are used and the thermal profile has a fundamental role.

Keywords:
Vegetable oil
Melting
Solid–liquid equilibrium
Interesterification
Simulation
Solid fat content

1. Introduction

Product design has been evaluated as one of the challenges that chemical engineering has to face to help industry meet market demands for value-added products showing a desired performance (Charpentier, 2002; Hill, 2009). Product development involving vegetable oils deals with a large combinatorial problem due the existence of a great variability of raw materials, the multiple ways of mixing them and the possibility of promoting reaction in a given mixture. There is an experimental effort to mix vegetable oils and promote chemical interesterification (CI) to achieve products with enhanced

nutritional characteristics while keeping physical properties within the desired range. Among these properties, the Solid Fat Content (SFC) is of great importance, as bulk physicochemical properties and sensory attributes of many products are determined by the fraction of the molecules (triacylglycerols) that are solidified at a given temperature. One such example is the food industry, in which the melting profile affect attributes such as texture, creaminess, hardness, taste and spreadability (Brapson-Danthine and Deroanne, 2004; Narine and Humphrey, 2004; Rousseau and Marangoni, 1998). When the SFC is low, the fat behaves as a viscous liquid (rather than a plastic material); on the other hand, when the SFC is greater than 15–20%, the molecular interactions between crystals lead to a plastic material, where the liquid oil is immobilized inside the crystalline network, retaining its consistency (Criado et al., 2008; da Silva et al., 2010).

The search for new mixtures of vegetable oils matching desired melting profiles and enhanced nutritional properties is usually based on design heuristics, prior experience and direct

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experimental studies, widely reported on literature. Despite the high number of these valuable experimental works, thermodynamic modeling and computational approaches are still scarce. The aim of the present work is to show how product design using vegetable oils can take advantage of computational tools and thermodynamic modeling. For this, the whole melting curves (SFC Vs. Temperature) and the effect of chemical interesterification on melting profile are predicted. The pre-experimental evaluation of a large set of vegetable oils and their blends, in different compositions and temperatures, allows the experimental efforts to be focused on the most promised formulations in terms of SFC. Margarine, modified butters, shortenings, cocoa butter replacements and structured lipids are some examples of areas that can take advantage of SFC predictions. In such products, new formulations must match a desired melting profile and minimizing experiments can reduce cost and time for product development.

2. Literature background on SLE modeling of fatty systems

The literature on the Solid Fat Content of fatty systems reports mainly experimental measurements. Concerning modeling, the main part of published works deal with fitting model parameters to Solid-Liquid Equilibrium (SLE) experimental data, mainly for binary mixtures of fatty acids (Inoue et al., 2004a, 2004b, 2004c) or triacylglycerols (Boodhoo et al., 2008). However, natural vegetable oils are far more complex as they can be composed of up to dozens of triacylglycerols (TAGs), which are 3 fatty acids esterified to the glycerol backbone. Therefore, the physical properties and Solid-Liquid Equilibrium of vegetable oils are due mainly to the inter and intramolecular interactions of TAGs, rather than to free fatty acids. Despite the recent studies in the modeling of binary mixtures (Rocha and Guirardello, 2009), there is a lack of predictive computational tools to handle the complexity of the problem in a multicomponent level using triacylglycerols as the representative molecules. Among the works dealing with SLE of triacylglycerols for multicomponent mixtures, one can highlight the works of Himawan et al. (2006), Wesdorp et al. (2005) and Won (1993), the first one being a review. The scarce experimental data on pure component properties, the high number of possible TAGs in a multicomponent mixture and the existence of polymorphic states on solid phase (α , β' and β) make the problem challenging.

There are three main Solid-Liquid Equilibrium models in current literature for fatty mixtures: Bragg-Williams approximation (Bragg and Williams, 1934), Slaughter and Doherty model (Slaughter and Doherty, 1995) and Margules-isomorphism correlations (Wesdorp et al., 2005).

- Bragg-Williams approximation assumes non-ideal mixing in both liquid and solid phases and attributes the non-ideality of mixing to the enthalpy term of the Gibbs free energy of mixing. It uses the parameters ρ_L and ρ_S fitted to experimental binary data, which are the energy differences between molecules pairs in solid and liquid phases. The works of Abes et al. (2007) and Boodhoo et al. (2008) follow this approach.
- Slaughter and Doherty model deals with compound-forming systems, assuming the formation of a stoichiometric compound in the solid phase and considering that the solid phases are almost immiscible.
- Concerning the Margules-isomorphism model, Wesdorp et al. (2005) collected a large set of experimental data and noticed that Margules interaction parameters were well-correlated to the degree of isomorphism between 2 TAGs. Applying Flory Huggins theory, they also concluded that the liquid phase could be considered ideal in most cases, except when a large

difference in molecular size occurs (differences in carbon number greater than 15–20). Regarding the solid phases, only the activity coefficients of the β' and β phases needed to be determined, whereas the solid α polymorph could be considered as ideal. That is a reasonable assumption because solid non-ideal behavior comes from a substantial distortion in the regular crystal lattice of a pure component by adding a molecule of another size. That distortion is not significant in a disordered state such as the α polymorph but must be accounted for in the denser packed β' and β systems Wesdorp et al. (2005).

Analyzing the current literature as a whole, one can say that the current approaches have the advantage of offering detailed descriptions of a specific binary mixture, enlarging the physical knowledge of such mixtures and offering experimental background for molecular structure-crystalline behavior relationships. For example, for a given binary mixture, works in literature identify different regions on the phase diagrams and make detailed descriptions of crystal morphology. However, the results are specific to that particular binary mixture. In the literature, there is a lack of tools that allow one to predict how changes in composition (e.g., enriching the blend with a given oil) or molecular structure (e.g., removing unsaturations) impact a fundamental property of interest for the industry (the SFC). This is particularly important for natural systems (vegetable oils) showing a high number of triacylglycerols.

After applying our approach to binary mixtures and to a single vegetable oil enhanced with a structured lipid (Teles dos Santos et al., 2010, 2011), we aim to evaluate the capability of this approach to cope with more complex mixtures. Different from current literature dealing with experimental data on SFC, the present work uses SLE modeling and computational tools to predict the melting curves (SFC Vs. Temperature) and predict how chemical interesterification influences the melting profile of vegetable oils blends.

3. Problem formulation

3.1. Solid-liquid equilibrium

In order to predict the SFC at a given temperature, one must solve a SLE problem. Due to their high molecular weight, TAGs tend to crystallize in 3 main crystalline networks (polymorphic forms): α , β' and β (Fig. 1). Further discussions about polymorphic states and solid-solid transitions can be found in Yano and Sato (1999) and Sato (2001).

The prediction of polymorphic states is not possible using equilibrium-based models, because the shape and size of crystals are related to kinetic factors of crystallization and process conditions. The objective of the present work is offer a predictive tool able to evaluate the solid/liquid ratio in an equilibrium state for each one of the three basic polymorphic forms of Fig. 1.

Computing the phase equilibrium is the solution of a nonlinear programming problem searching for the minimization of the Gibbs free energy (G), subject to linear material balance constraints. The problem can be stated as:

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

s.t:

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

$$0 \leq n_i^j \leq n_i \quad i = 1 \dots nc; j = 1 \dots np \quad (3)$$

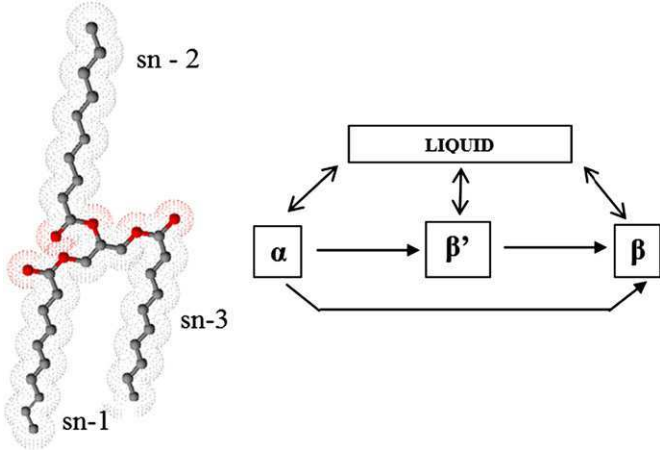


Fig. 1. Example of molecular structure and main solid-liquid phase transitions in triacylglycerols. sn: stereospecific numbering.

where nc and np are the number of different 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 . 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 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:

$$g^j = \sum_{i=1}^{nc} x_i^j (\bar{g}_i^j) \quad (4)$$

where x_i^j is the molar fraction of TAG i in phase j . By definition, the partial Gibbs Energy of a component in a mixture is the chemical potential of that component. Eq. (4) can be rewritten as:

$$g^j = \sum_{i=1}^{nc} x_i^j (\mu_i^j) = > g^j = \sum_{i=1}^{nc} x_i^j (\mu_{i,0}^j + RT \ln \gamma_i^j x_i^j) \quad (5)$$

where $\mu_{i,0}^j$ is the chemical potential of a pure TAG i in the j state in the same temperature of the mixture (T) and γ_i^j the activity coefficient of TAG i in phase j .

3.1.1. For j =liquid

In the reference state of pure liquid, chemical potential is zero. Also, the liquid phase is treated as ideal (See Section 2). This leads to the following simplification on Eq. (5):

$$g^{\text{liquid}} = RT \sum_{i=1}^{nc} (x_i^{\text{liquid}} \ln x_i^{\text{liquid}}) \quad (6)$$

3.1.2. For j =solid (α , β' or β)

The chemical potential of a pure component i in the solid state in the temperature of the mixture (T) is given by:

$$\mu_{i,0}^{\text{solid}(j)} = T \Delta H_{m,i}^{\text{solid}(j)} \left(\frac{1}{T} - \frac{1}{T_{m,i}^{\text{solid}(j)}} \right) \quad (7)$$

where $T_{m,i}^{\text{solid}(j)}$ and $\Delta H_{m,i}^{\text{solid}(j)}$ are the melting temperature and melting enthalpy of pure TAG i considering the solid state j .

Using Eq. (7) on Eq. (5), one have for the solid phases:

$$g^{\text{solid}(j)} = RT \sum_{i=1}^{nc} x_i^{\text{solid}(j)} \left(\frac{\Delta H_{m,i}^{\text{solid}(j)}}{R} \left(\frac{1}{T} - \frac{1}{T_{m,i}^{\text{solid}(j)}} \right) + \ln (\gamma_i^{\text{solid}(j)} x_i^{\text{solid}(j)}) \right) \quad (8)$$

($j = \alpha, \beta'$ or β)

Therefore, $G(n)$ on Eq. (1) can be calculated using Eq. (6) (liquid) and Eq. (8) (solid). The decision variables are the number of mols of each component i in each phase j (n_i^j), in order to obtain the minimum of the total Gibbs Free Energy (G) in a given temperature (T). Two sets of data are, however, necessary:

An Excess Gibbs Free Energy model to compute the activity coefficients on the non-ideal solid phases:

$$\gamma_i^{\text{solid}(j)}, j = \alpha, \beta' \text{ or } \beta$$

Melting temperature and melting enthalpy of each TAG in each crystalline state:

$$\Delta H_{m,i}^{\text{solid}(j)} \text{ and } T_{m,i}^{\text{solid}(j)}, j = \alpha, \beta' \text{ or } \beta$$

3.1.3. Excess Gibbs free energy model

The thermodynamic model used in this work is the 2-suffix Margules model, due to three reasons: (1) It is suitable for mixtures formed by components with similar molecular volume, shape and chemical nature (Prausnitz et al., 1999); (2) There are experimental data for triacylglycerols available in literature that were used to develop correlations between the binary interaction parameters ($A_{ij}(\beta')$ and $A_{ij}(\beta)$) and the geometrical similarity in the pair i - j . This similarity is expressed in terms of the differences in the size of fatty acids chains (Wesdorp et al., 2005) and (3) It allows the flexibility/simplicity required in the optimization step of this work. Appendix A details how the interaction parameters are predicted.

3.1.4. Melting temperature and melting enthalpy

For each TAG, 6 values are required: 3 values of melting enthalpies and 3 values of melting points (each one corresponding to a solid-liquid transition in Fig. 1). 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 3 polymorphic states. In such cases, the predictive methods of Zeberg - Mikkelsen and Stendby, 1999 and Wesdorp et al. (2005) are used.

3.2. 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 module was then coupled with the main program written in FORTRAN 90, which handles the calculation of interaction parameters, melting temperature and melting enthalpy and the generation of triacylglycerols from fatty acids data. The SLE was then solved over a temperature range: starting from a minimal temperature at which the SFC is 1, the temperature is increased until complete melting (SFC=0). Each new optimization problem at T_i is solved using the previous results (at T_{i-1}) as starting point. 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 at the given temperature. When spanning a temperature range, the whole melting curve can be computed. Also, using the numerical differentiation of Excess

Gibbs Energy calculated at each temperature, it is possible to compute Differential Scanning Calorimetry curves based on equilibrium hypotheses (Teles dos Santos et al., 2011,2012).

3.3. Simulation of blending and chemical interesterification (CI)

If two or more vegetable oils are simply mixed, the TAG composition of the mixture is calculated using a simple mass balance on each TAG present on the starting vegetable oils. Experimentally, by the action of heat and catalyzers (chemical interesterification), the fatty acids present in this initial mixture can be redistributed randomly on the three positions of the glycerol, originating a new TAG profile. Because the TAG profile is changed, the blend shows different physical properties after reaction (including melting profile). In order to compute this TAG profile after reaction (simulating the reaction), the computational program makes a random distribution of fatty acids present on the original oils in the glycerol backbone. This is a combinatorial problem and it is further detailed on Appendix B.

The two procedures (blending vegetable oils and promoting chemical interesterification) are widely used in experimental researches and in the industrial sector. The objective of such techniques is to change the composition in terms of triacylglycerols and, therefore, to achieve enhanced physical and nutritional properties in relation to the original raw materials. Fig. 2 summarizes how the computational approach of this work simulates the experimental steps normally used in product development.

In this work, the term “before reaction” refers to the simple mixture of the concerned vegetable oils; the term “after reaction” refers to the product of the chemical interesterification of this mixture.

4. Results

The methodology was applied to 6 different blends of vegetable oils formed by canola oil (CO) *Brassica napus*, fully hydrogenated palm oil stearin (FHPOS), palm oil stearin (POS) and cottonseed oil (CSO).

All computational times reported in this work refers to a PC Intel(R) Core(TM)2 Quad processor, CPU Q9550 2.83 GHz each and 2.00 GB of RAM, operational system Windows Vista 32 bits.

4.1. Preliminary selection of a threshold mass fraction

Mixing vegetable oils leads to a system with a large number of TAGs. The simplest natural vegetable oils have 6 to 8 fatty acids (ex. Palm stearin and canola oil). If one considers a 50–50% mixture of these two vegetable oils, 92 different TAGs can be theoretically formed. However, many TAGs show an insignificant fraction of total composition. Table 1 shows the composition ranges and the corresponding number of TAGs for this palm stearin–canola oil mixture.

One can notice that, despite the large number of possible TAGs (92), only 2 TAGs have a mass fraction greater than 10%. The other TAGs, despite their small individual fraction, have together a significant influence on the blend properties: the remaining 90 TAGs account for 74.43% in mass of the mixture.

It is important that the optimization algorithm takes into account a sufficient number of the TAGs generated computationally in order to obtain an expressive mass fraction of the mixture. However, a trade-off arises: the higher the number of TAGs considered the better the mixture is represented, but the computational time increases and uncertainties on pure component properties predictions become more critical. In the above case (92 TAGs), a total of 552 pure component properties (92×6) must be known or calculated.

In the case of chemical interesterification (CI), this issue is even more critical. The goal of CI is a random redistribution of fatty acids, so an important consequence of CI (and this is what makes it different from enzymatic interesterification) is the formation of a higher number of TAGs from a mixture in which this number is already large.

Table 1
Mass fraction and corresponding number of TAGs.
Mixture: palm oil stearin–canola oil 50–50.

Composition range x (% mass)	Number of TAGs
$x \leq 0.01$	43
$0.01 < x \leq 1$	31
$1 < x \leq 10$	16
$x > 10$	2
Total	92

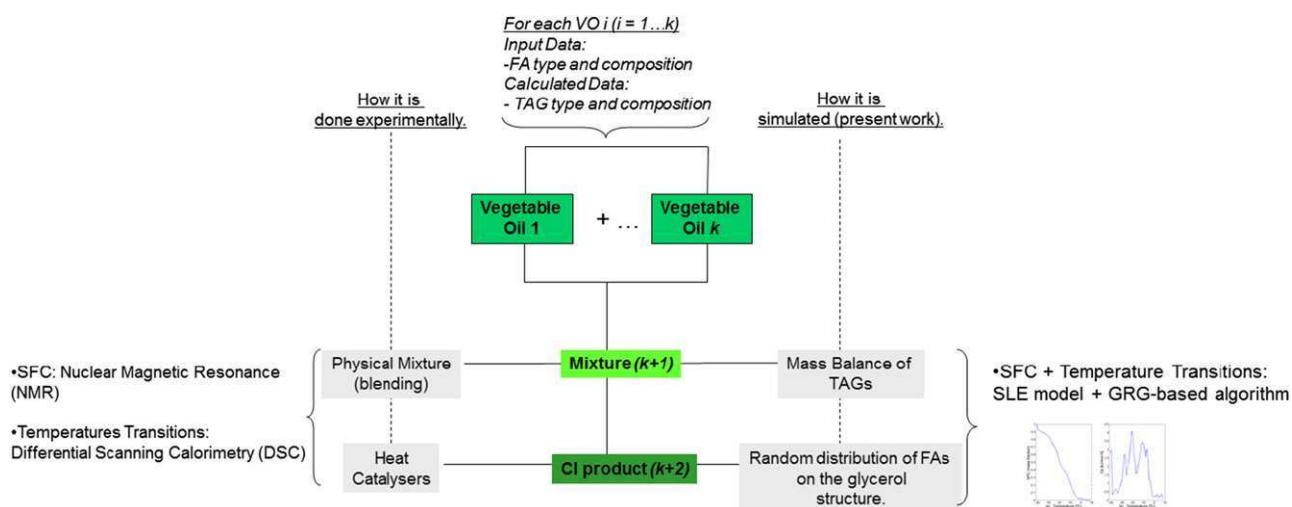


Fig. 2. Simulated (this work) Vs. common experimental procedures for mixing and reaction of vegetable oils. VO: vegetable oil; FA: fatty acid; TAG: triacylglycerol; SLE: solid–liquid equilibrium; SFC: solid fat content; CI: chemical interesterification; GRG: generalized reduced gradient.

Table 2 shows the number of TAGs computationally generated for both cases: before reaction and after reaction. These results reinforced what was discussed earlier: the thermodynamic model must be kept as simple as possible, as the computational efforts must be oriented to the optimization step. For all systems discussed in this work, the whole set of triacylglycerols predicted from fatty acid data is available as [supplementary data](#) (BinaryBlends_TAGs.xls file).

Despite the formation of a large number of TAGs, these components are very similar regarding chemical nature. The differences rely on the size of fatty acid chains and degree of unsaturation. Fig. 3(a) shows the mass fraction of each molecule present on the blend CO–FHPOS 30/70 before and after reaction. One can notice that few TAGs (about 10) have a concentration greater than 5%. Fig. 3(b) shows the cumulative concentration of those TAGs. For a given mass fraction of the mixture, the corresponding number of TAGs that must be considered is always larger after reaction (interesterified blends), due to the formation of additional TAGs by the redistribution of fatty acids. As an example, before CI reaction, the 10 first TAGs represent 80% in mass of the blend. After CI reaction, the first 10 TAGs represent less than 60% in mass (Fig. 3(b)).

The following question arises: how many of the TAGs generated by the program are needed to describe properly the mixture, and therefore must be used in the SLE model? Several tests were performed to obtain the cut-fraction necessary to describe satisfactorily the blend properties. These tests suggest that a number of TAGs accounting for 85% in mass should be used. This mass fraction (85%) must be adjusted on experimental data for other mixtures, but when no experimental data is available, the value of 85% in mass is suggested. Fig. 4 shows the predicted melting curve for the CO–FHPOS 30/70 mixture before reaction and the influence of the number of TAGs used. The covered mass fraction of the blend in each case and the corresponding computational time are also indicated. One can observe that the best representation of experimental data was obtained using 13 TAGs. The use of

Table 2
Theoretical number of TAGs before and after chemical interesterification reaction.

Blend	Number of TAGs (before reaction)	Number of TAGs (after reaction)
CO–FHPOS 30/70	96	162
CO–FHPOS 70/30	99	151
CO–POS 50/50	92	98
CO–POS 60/40	92	103
CO–POS 40/60	107	122
CSO–POS 70/30	93	100

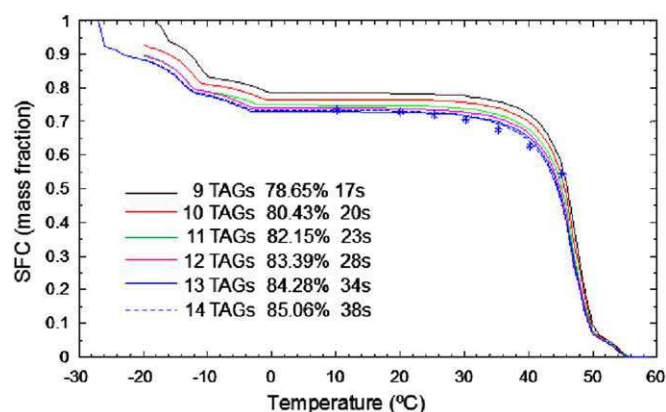


Fig. 4. Simulated melting curves for the blend CO–FHPOS 30/70 before chemical interesterification reaction. Influence of number of TAGs used in predictions along with corresponding mass fraction and computational time. Experimental data (*) from Karabulut et al. (2004).

14 TAGs does not increase the performance and requires 10% more computational time. Indeed, the 14th TAG corresponds to only 0.078% in mass of the mixture.

4.2. Binary blends

The SFC predictions were systematically compared with experimental data taken from literature (Karabulut et al., 2004). Different blends were used to simulate the whole melting curve before and after CI reaction. Table 3 summarizes the number of TAGs, the corresponding mass fraction, the polymorphic state used in each case and the computational time used to simulate the whole melting. In all the presented curves, the temperature increment is 1 °C. The details brought by smaller values are unnecessary to describe the global behavior and the computational time increases substantially.

4.2.1. CO–FHPOS (canola oil—fully hydrogenated palm oil stearin)

For the blend CO–FHPOS 30/70 (Fig. 5), the computational results performed better before the reaction than for the interesterified product (after reaction). One can also notice that the CI reaction reduces the SFC in the whole range of experimental data (10 to 45 °C). However, the model predicts a higher SFC for the system after reaction at temperatures lower than 10 °C.

Fig. 6 shows the simulated melting curves for the blend CO–FHPOS 70/30 before and after CI reaction. It can be noted that the SFC of this blend is lower than the SFC of the previous blend, formed by the same vegetable oils but with inverse composition: 70% of CO and 30% of FHPOS. This is due to the higher amount of the low-melting point component (canola oil). Despite the larger deviation from experimental point at 10 °C after reaction, the model was able to identify 2 characteristics revealed by experimental data:

For simple mixture (before reaction), the SFC varies slowly with temperature, remaining in about 30% in the range –5 °C to 25 °C, following a steep reduction above 35 °C.

After reaction, the final melting point is lower than that of the system before reaction, showing a continuous decreasing in SFC with temperature until final melt (35 °C experimental, 40 °C calculated).

The reduction on SFC after reaction is due to the reduction of trisaturated TAGs (higher melting point). This reduction is caused by the redistribution of fatty acids and the formation of a high

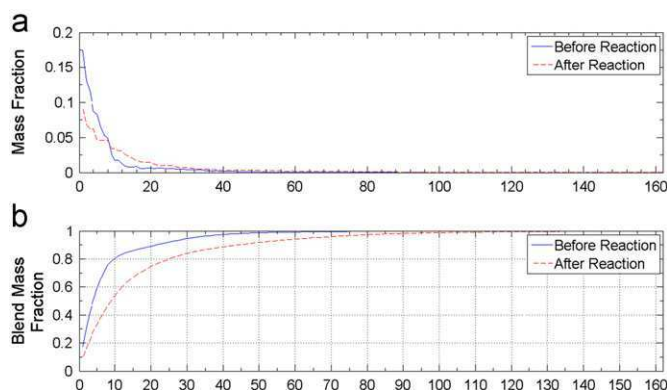


Fig. 3. (a) Calculated mass fraction of each TAG present in the blend CO–FHPOS 30/70 before and after reaction. (b) Number of TAGs and corresponding mass fraction of the blend CO–FHPOS 30/70 before and after reaction.

Table 3

Number of TAGs, corresponding mass fraction, polymorphic state and computational time for different blends, before and after chemical interesterification reaction.

Blend	Before reaction				After reaction			
	Number of TAGs used	Mass fraction (%)	Polymorph	Time	Number of TAGs used	Mass fraction (%)	Polymorph	Time
CO-FHPOS 30/70	13	84.28	β'	31 s	30	83.96	β'	1 min 9 s
CO-FHPOS 70/30	15	81.38	β'	36 s	30	80.65	β	3 min 56 s
CO-POS 50/50	15	80.13	β	1 min 23 s	20	83.78	β'	32 s
CO-POS 60/40	20	86.73	β	1 min 50 s	30	91.79	β'	54 s
CO-POS 40/60	30	93.53	β	7 min 20 s	34	93.15	β'	1 min 37 s
CSO-POS 70/30	20	89.78	β	2 min 16 s	23	91.83	β'	1 min 11 s

CO: canola oil; FHPOS: fully hydrogenated palm oil stearin; POS: palm oil stearin; CSO: cottonseed oil.

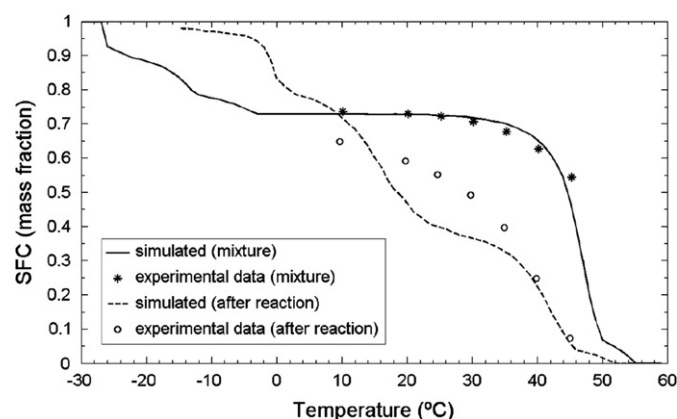


Fig. 5. Melting curves for the blend CO-FHPOS 30/70 before (mixture) and after chemical interesterification reaction.

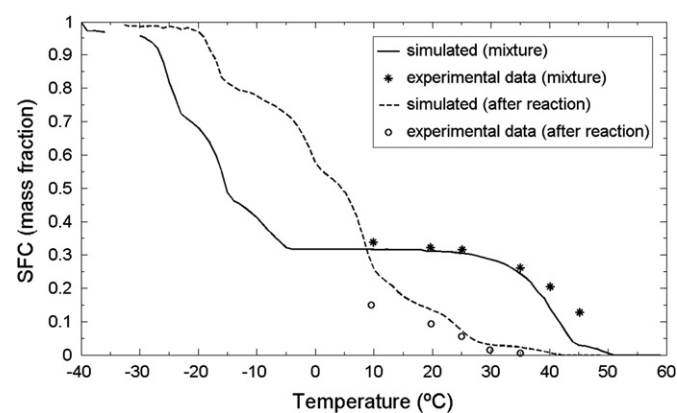


Fig. 6. Melting curves for the blend CO-FHPOS 70/30 before (mixture) and after chemical interesterification reaction.

number of other triacylglycerols with lower melting point, not present in the original blend. In order to illustrate this point, Table 4 shows the 13 TAGs used to represent the system before reaction and the 30 TAGs used to represent the product of CI reaction on the blend CO-FHPOS 30/70. One can notice that the mass fraction of the TAG with higher melting point (composed of 3 stearic acids, SteSteSte) is reduced from 4.92% to 2.53%. The same occurs for all other saturated TAGs: all of them have their contribution on the mixture reduced.

Another issue coming up from the simulated curves is the existence of the iso-solid point, the temperature in which the SFC after reaction is equal to the SFC before reaction (Figs. 5 and 6). The experimental literature also reports such cases (Ahmadi et al., 2008). This point indicates that it is useless to promote reaction between the vegetable oils if one wants to change the SFC at this

Table 4

Predicted composition in triacylglycerols before and after interesterification reaction (CO/FHPOS 30-70).

Before reaction			After reaction		
Triacylglycerol	Molar fraction	Mass fraction	Triacylglycerol	Molar fraction	Mass fraction
Pam Pam Ste ^a	0.1746	0.1744	Pam Pam Ste ^a	0.0942	0.0927
Pam Ste Ste ^a	0.1270	0.1311	Pam Ste Ste ^a	0.0674	0.0685
Pam Pam Pam ^a	0.1201	0.1159	Pam Pam Pam ^a	0.0659	0.0626
Pam Ste Pam ^a	0.0873	0.0872	Pam Pam Ole	0.0636	0.0624
Ole Ole Ole	0.0824	0.0829	Pam Ste Pam ^a	0.0471	0.0463
Ste Pam Ste ^a	0.0635	0.0656	Pam Ste Ole	0.0455	0.0461
Ole Ole Lin	0.0532	0.0535	Pam Ole Ste	0.0455	0.0461
Ste Ste Pam ^a	0.0462	0.0492	Ste Pam Ole	0.0455	0.0461
Ole Lin Ole	0.0266	0.0267	Ste Pam Ste ^a	0.0337	0.0343
Ole Ole aLnn	0.0177	0.0178	Ste Ste Ole	0.0325	0.0341
Ole Lin Lin	0.0172	0.0172	Pam Ole Pam	0.0318	0.0312
Pam Ole Ole	0.0127	0.0124	Pam Ole Ole	0.0307	0.0311
Ole aLn Ole	0.0089	0.0089	Ste Ste Ste ^a	0.0241	0.0253
Total	0.8374	0.8428	Ste Ole Ole	0.0220	0.0230
			Pam Pam Lin	0.0206	0.0201
			Ste Ole Ste	0.0163	0.0170
			Ole Pam Ole	0.0154	0.0155
			Pam Ste Lin	0.0147	0.0149
			Pam Lin Ste	0.0147	0.0149
			Ste Pam Lin	0.0147	0.0149
			Ole Ste Ole	0.0110	0.0115
			Ste Ste Lin	0.0105	0.0110
			Pam Lin Pam	0.0103	0.0101
			Pam Ole Lin	0.0099	0.0100
			Pam Lin Ole	0.0099	0.0100
			Ole Pam Lin	0.0099	0.0100
			Ole Ole Ole	0.0074	0.0077
			Ste Ole Lin	0.0071	0.0074
			Ste Lin Ole	0.0071	0.0074
			Ole Ste Lin	0.0071	0.0074
			Total	0.8361	0.8396

^a Saturated TAG present before CI. Pam: palmitic acid (C16:0); Ste: stearic acid (C18:0); Ole: oleic acid (C18:1); Lin: linoleic acid (C18:2); aLn: linolenic acid (C18:3).

temperature. The possibility of identifying such points computationally can avoid unpromising experiments.

4.2.2. CO-POS (canola oil-palm oil stearin)

The model was able to describe properly the melting profile before and after CI reaction, especially the blend CO-POS 50/50 (Fig. 7) and 40/60 before reaction (Fig. 9). For the blend CO-POS 40/60, the optimization step did not converge to a solution at around -19°C , which did not compromise the melting curve profile. Meaningful information arises from these simulated curves. On the blend CO-POS 40/60, a higher SFC is expected than in the blend CO-POS 50/50. This last one is in turn expected to have a higher SFC than the blend CO-POS 60/40, as the fraction

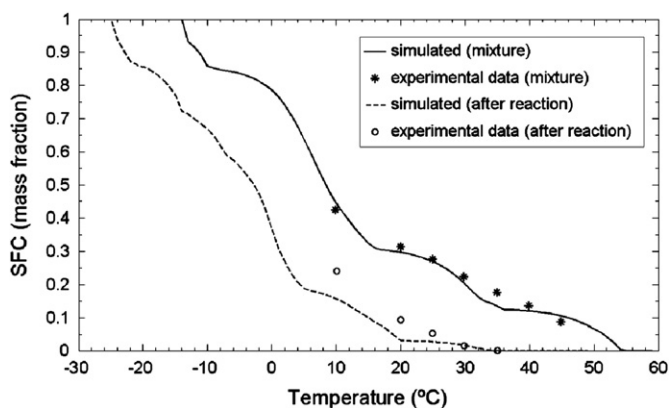


Fig. 7. Melting curves for the blend CO-POS 50/50 before (mixture) and after chemical interesterification reaction.

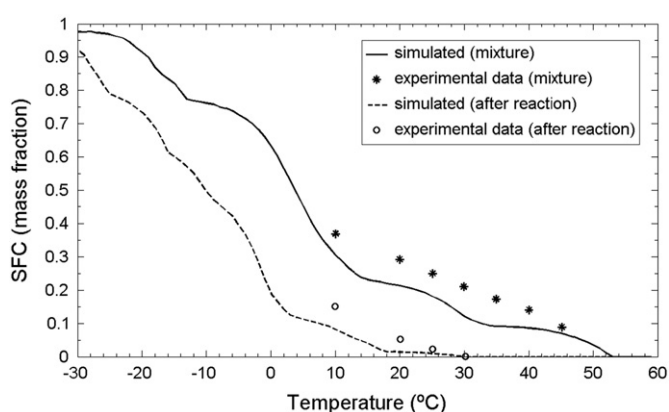


Fig. 8. Melting curves for the blend CO-POS 60/40 before (mixture) and after chemical interesterification reaction.

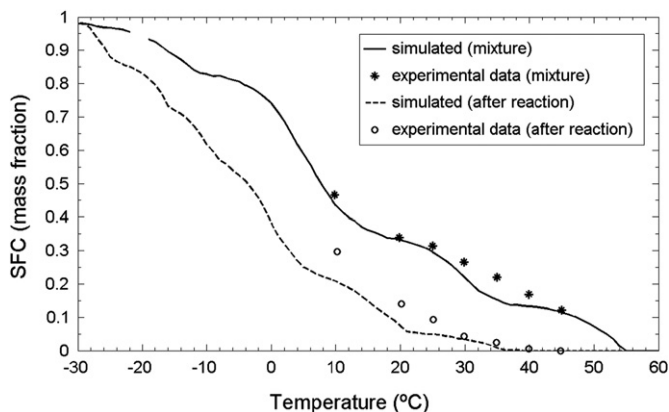


Fig. 9. Melting curves for the blend CO-POS 40/60 before (mixture) and after chemical interesterification reaction.

of the higher-melt vegetable oil is reduced (POS). Figs. 7–9 confirm this fact. As an example, we have at 25 °C (before reaction): SFC=31% (CO-POS 40/60), SFC=28% (CO-POS 50/50) and SFC=19% (CO-POS 60/40). However, the final melting point is not changed (55 °C, 55 °C and 53 °C, respectively). This shows that formulations with similar final melting points can have different melting profiles at the usage temperature, which influences attributes such as consistency.

Blends with FHPOS have higher SFC at a given temperature when compared to blends with POS, as the hydrogenation process

eliminates the unsaturations and, as consequence, increases the melting point of TAGs present in POS.

One important characteristic differentiates the blends composed of FHPOS and the blends composed of POS before reaction: the former shows a small variation of SFC between 10 and 40 °C (Figs. 5 and 6), followed by a steep reduction after 40 °C; in the last ones, the variation of SFC is steep in the whole experimental temperature range (Figs.7–9). These predicted results were also observed experimentally (Karabulut et al., 2004). It must be highlighted that besides SFC, the sharpness of the melting range, along with other factors, determines the range within which a fat can be considered plastic (Rao et al., 2001).

4.2.3. CSO-POS (cottonseed oil-palm oil stearin)

This blend is well described by the computational approach, both before and after CI reaction. No iso-solid point was detected over the melting range, as in the case of CO-POS blends. Fig. 10 shows the melting curves for the blend 70/30 of these two fats, before and after CI reaction.

Table 5 summarizes the average absolute error (AAE) between predicted and experimental SFC for the six blends showed in Figs.5–10.

4.2.4. Milkfat-corn oil

In order to further compare predicted and experimental data, the present methodology was tested on a system with higher complexity in terms of TAGs: interesterified milkfat-corn oil 80/20 (145 different TAGs, theoretically predicted by the random distribution of fatty acids). The fatty acids composition of individual fats and experimental SFC were obtained after Rodrigues and Gioielli (2003). The results are shown on Fig. 11.

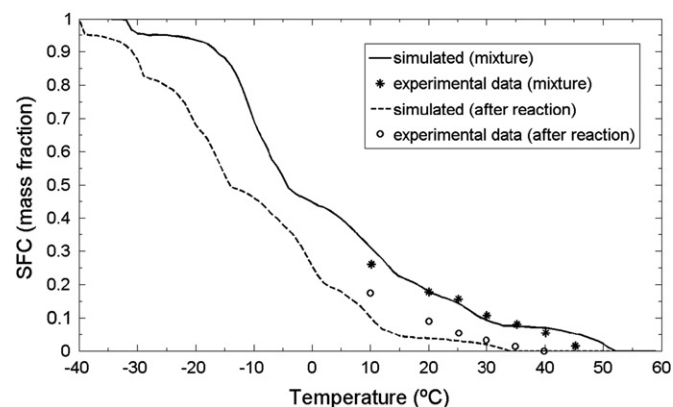


Fig. 10. Melting curves for the blend CSO-POS 70/30 before (mixture) and after chemical interesterification reaction.

Table 5

Average absolute error in solid fat content for the blends, before and after chemical interesterification reaction.

Blend	AAE (%)	
	Before reaction	After reaction
CO-FHPOS 30/70	2.23	8.12
CO-FHPOS 70/30	3.75	3.93
CO-POS 50/50	2.07	3.46
CO-POS 60/40	6.69	3.16
CO-POS 40/60	3.27	3.10
CSO-POS 70/30	1.96	3.08

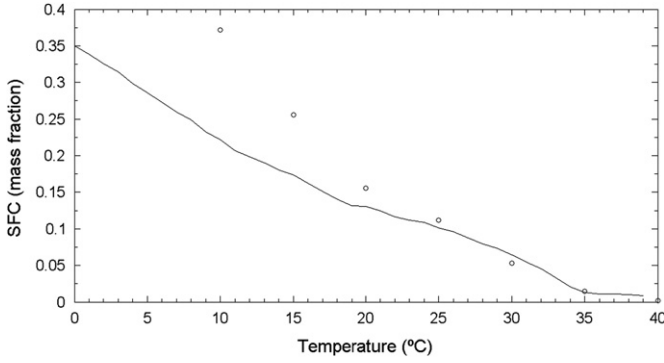


Fig. 11. Simulated melting curve for the blend milkfat-corn oil 80/20 after chemical interesterification reaction. Experimental data (°) from Rodrigues and Gioielli (2003).

It can be noted that, although the higher number of TAGs for this system (145), the model was able to predict the SFC with high accuracy in temperatures above 20 °C. However, the model shows less accurate predictions compared with 2 experimental points: at 10 °C and 15 °C. One possible reason to this is that some TAGs have their melting temperature (T_m) underpredicted. So, the SFC is underestimated below 20 °C. At higher temperatures, these TAGs are in liquid phase and the errors in melting point predictions for pure TAGs do not influence the SFC. As the experimental melting point for all 145 TAGs is not known, it was not possible to identify which ones show larger deviations.

If we consider the temperature range above 15 °C, the average absolute error (AAE) over the 5 points is 1.04% in SFC. If the whole temperature range is considered, AAE=4.03%. Taking into account the 6 blends evaluated before reaction and the 7 blends evaluated after reaction, the average absolute errors are 3.33% and 4.13%, respectively.

5. Conclusions

The computational approach using Solid-Liquid Equilibrium modeling and optimization tools revealed the feasibility in predicting the melting profile of binary blends composed of canola oil, fully hydrogenated palm oil stearin, palm oil stearin, cottonseed oil, milkfat fat and corn oil. The chemical interesterification can be simulated as well, using a random distribution of fatty acids on the glycerol backbone in order to determine the TAG composition after reaction. The predicted results revealed a good agreement in qualitative and quantitative aspects when compared to experimental data gathered from literature for these systems. The predictive nature of the methodology encourages its use in other systems composed of triacylglycerols. The present approach is based on equilibrium hypotheses and no time-dependent properties or detailed solid state description is possible. This is not a drawback however, as the main objective is the pre-experimental evaluation of a large set of vegetable oils, in different compositions and temperatures, allowing the experimental efforts to be focused on the most promising formulations in terms of SFC.

Appendix A. Excess Gibbs free energy and binary interaction parameter Models

The definition of activity coefficient is given by:

$$RT \ln \gamma_i(T, P, x) = \bar{g}_i^E = \left(\frac{\partial n g^E}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (\text{A1})$$

The 2-suffix Margules equation for multicomponent mixtures is given by:

$$g^E = \sum_{i=1}^{nc} \sum_{j=i+1}^{nc} A_{ij} x_i x_j \quad (\text{A2})$$

$$A_{ij} = 2q a_{ij} \quad (\text{A3})$$

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 parameter a_{ij} is related to the interactions between TAGs i and j (Prausnitz et al., 1999). nc is the number of TAGs in the mixture. The work of Wesdorp et al. (2005) showed that there is a strong correlation between the coefficient of geometrical similarity (isomorphism) and the parameter A_{ij} . This isomorphism (ε) between two TAGs can be described by the following expression:

$$\varepsilon = 1 - \frac{v_{non}}{v_0} \quad (\text{A4})$$

where v_{non} is the sum of absolute differences on carbon number (nc) of the fatty acids chains in the pair i - j , considering the 3 stereo-positions (sn).

$$v_{non} = \sum_{k=1}^3 |nc^i(sn^k) - nc^j(sn^k)| \text{ for a given pair of TAGs } i \text{ and } j \quad (\text{A5})$$

v_0 is the sum of the carbon numbers of the smallest chain (comparing the 2 molecules of the pair i - j), considering the 3 stereo-positions (sn).

$$v_0 = \sum_{k=1}^3 \min(nc^i(sn^k), nc^j(sn^k)) \text{ for a given pair of TAGs } i \text{ and } j \quad (\text{A6})$$

The linear regression of experimentally determined parameters A_{ij} with the corresponding isomorphism led to the following correlations (Wesdorp et al., 2005):

$$\varepsilon > 0.93 : \frac{A_{ij}^\beta}{RT} = 0 \text{ (high molecular similarity; complete miscibility)} \quad (\text{A7})$$

$$\varepsilon \leq 0.93 : \frac{A_{ij}^\beta}{RT} = -19.5\varepsilon + 18.2 \quad (\text{A8})$$

$$\varepsilon > 0.98 : \frac{A_{ij}^\beta}{RT} = 0 \text{ (high molecular similarity; complete miscibility)} \quad (\text{A9})$$

$$\varepsilon \leq 0.98 : \frac{A_{ij}^\beta}{RT} = -35.8\varepsilon + 35.9 \quad (\text{A10})$$

Therefore, the parameters of the model (A_{ij}) can be predicted from the number of carbons on each fatty acid chain. The primary value of the Margules equations lies in their ability to serve as simple empirical equations for representing experimentally determined activity coefficients with only a few constants and when experimental data are scattered and scarce, they serve as an efficient tool for interpolation and extrapolation with respect to composition (Prausnitz et al., 1999).

Appendix B. Simulation of chemical interesterification (CI)

By means of heat and catalysts, the fatty acids present in a mixture of triacylglycerols can be reorganized in the glycerol structures. However, the reaction offers little or no control over the positional distribution of fatty acids in the final product,

Table B1

Triacylglycerols that can be formed in a system composed of 30% of oleic acid (Ole), 60% of palmitic acid (Pam) and 10% of stearic acid (Ste).

TAG number	TAG code	Molar fraction
1	OleOleOle	0.027
2	OleOlePam	0.108
3	OleOleSte	0.018
4	OlePamOle	0.054
5	OlePamPam	0.216
6	OlePamSte	0.036
7	OleSteOle	0.009
8	OleStePam	0.036
9	OleSteSte	0.006
10	PamOlePam	0.108
11	PamOleSte	0.036
12	PamPamPam	0.216
13	PamPamSte	0.072
14	PamStePam	0.036
15	PamSteSte	0.012
16	SteOleSte	0.003
17	StePamSte	0.006
18	SteSteSte	0.001

contrary to the enzymatic reaction (Willis and Marangoni, 1999). This means that a random distribution of fatty acids can describe the reaction product (no preferential position). The present approach assumes the hypotheses that the CI reaction is carried out until equilibrium, corresponding to a total random redistribution of fatty acids.

Therefore, the molar fraction of any TAG formed by the fatty acids j , l and m is calculated by the following expressions:

$$x_{jlm} = 2x_j x_l x_m \text{ for } j \neq m \text{ (possible } j = l \text{ or } m = l) \quad (\text{B1})$$

$$x_{jij} = (x_j)^2 x_l \text{ (possible } j = l) \quad (\text{B2})$$

where x_j is the overall molar fraction of fatty acid j . For example, in a system composed of 30% of oleic acid (Ole), 60% of palmitic acid (Pam) and 10% of stearic acid (Ste):

$$X_{\text{StePamOle}} = 2 \cdot (0.1)(0.6)(0.3) = 0.0360$$

$$X_{\text{SteOleOle}} = 2 \cdot (0.1)(0.3)(0.3) = 0.0180$$

$$X_{\text{PamOlePam}} = (0.6)^2(0.3) = 0.1080$$

$$X_{\text{PamPamPam}} = (0.6)^2(0.6) = 0.2160$$

The whole set of possible TAGs that can be theoretically formed in this case is show on Table B1.

Thus, if the overall fatty acid profile of the vegetable oils is known, the product of chemical interesterification can be estimated using the random model of fatty acids position on the triacylglycerols.

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