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Ternary Blends of Vegetable Oils: Thermal Profile Predictions for Product Design

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Abstract

This work deals with Product Design by means of theoretical predictions of the Solid Fat Content of different formulations using 3 vegetable oils. A Soli-Liquid Equilibrium (SLE) model was implemented and integrated into an optimization algorithm based on the Generalized Reduced Gradient method. A total of 3,696 SLE problems are solved, covering 57 binary blends, 3 pure vegetable oils and 171 ternary blends problems, before and after chemical interesterification reaction and at 8 different temperatures. A combinatorial random distribution of fatty acids in the glycerol structure is used to simulate the effect of the reaction. The results were compared with 256 experimental points, giving an average absolute error of 5.4 and 4.4 in Solid Fat Content for systems before and after reaction, respectively. Computer-aided tools can be useful to deal with the large combinatorial problem faced by product design, especially when desired product performance is related to a phase behavior in multicomponent mixtures.

Keywords: vegetable oil, product design, solid-liquid equilibrium, lipids.

1. Introduction

The interest in Chemical Product Engineering is a consequence in the shift in the chemical industry towards high value-added products, in which performance plays a major role (Hill, 2009). Among those products, cosmetics and foods are of great economic importance and have vegetable oils in their composition. In these products, the desired attributes (performance) are directly related to a solid-liquid phase behavior in a multicomponent mixture of triacylglycerols, the major compounds in vegetable oils. The use of computer-aided tools in lipid-based industry has attracted attention in Process System Engineering community. Examples of recent improvements concern property prediction models (Cunico et al., 2013), molecular dynamics (Brasiello et al., 2010), simulation of melting curves (Teles dos Santos et al., 2010) and studies about solid-liquid phase transitions in fatty compounds (Robustillo et al., 2014). Despite the increasing number of experimental and modeling studies in binary/ternary mixtures of fatty compounds, the melting behavior of multicomponent mixtures (blends of vegetable oils) is less studied in a computational point of view. This work aims to cope with this gap. When using vegetable oils for Product Design, the desired performance is related to a solid-liquid phase behavior, as in the case of the food industry where the Solid Fat Content (SFC) is a key property for match desired attributes (e.g. texture, creaminess). This work deals with theoretical predictions of SFC for Product Design using different formulations composed of 3 vegetable oils. The aim is to aid the decision-making process in choosing the best formulation in terms of desired SFC.

2. Models

2.1. Solid-Liquid Equilibrium Problem

About 95 % of vegetable oils are composed of triacylglycerols (TAGs), formed by 3 fatty acids sterified to a glycerol structure. As one TAG can be formed by 1, 2 or 3 different fatty acids, and even the position of these fatty acids leads to different TAGs, many TAGs molecules can be theoretically formed by only few fatty acids. Figure 1 shows a typical TAG molecular shape with the possible solid-liquid transitions including polymorphism in solid state (α , β' and β). To predict the solid/liquid ratio given the fraction of each vegetable oil in the blend and the temperature, a phase equilibrium problem is solved as 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:

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

s.t:

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

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

Where nc and np are respectively the number of different TAGs and the number of phases in the mixture; n_i^j and g_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 . TAG molecules can crystallize in 3 main crystalline states: α , β' and β . When a particular polymorphic state is evaluated, another constraint is added: the number of mols of all species in the other two polymorphic states is set to zero. Then, the optimization algorithm searches for the distribution of molecules between the solid and liquid phases that minimizes the Gibbs Free Energy. The decision variables are the number of mols of each component i in each phase j (n_i^j).

2.2. Thermodynamic Model

2.2.1. Liquid Phase

Previous literature works concluded that the liquid phase can be treated as ideal, based on the Flory Huggins theory (Wesdorp, 1990). Setting the reference state of pure liquid (chemical potential zero), we have for the liquid phase:

$$g^{\text{liquid}} = RT \sum_{i=1}^{nc} k_i^{\text{liquid}} \ln x_i^{\text{liquid}} \quad (4)$$

2.2.2. Solid Phases

The expression of the Gibbs Energy in solid phases is given by Eq.(5) (Prausnitz et al., 1999):

$$g^{\text{solid}(j)} = RT \sum_{i=1}^{nc} x_i^{\text{solid}(j)} \left[\frac{h_{m,i}^{\text{solid}(j)}}{R} - \frac{1}{T_{m,i}^{\text{solid}(j)}} \right] + \sum_{i=1}^{nc} x_i^{\text{solid}(j)} g_i^{\text{solid}(j)} \quad (5)$$

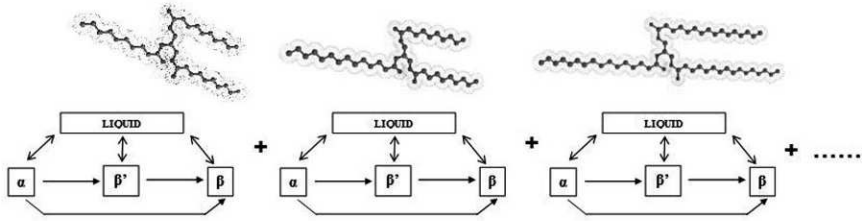


Figure 1. Typical triacylglycerol structures and possible solid-liquid phase transitions.

Where $\Delta H_{m,i}^{\text{solid}(j)}$ and $T_{m,i}^{\text{solid}(j)}$ are respectively the melting enthalpy and melting temperature of TAG i in solid state j and γ_i the activity coefficient of i on phase j .

2.3. Excess Gibbs Energy Model

The 2-suffix Margules model was chosen for three reasons: 1- it is suitable for mixtures where the components have similar molar volume, shape and chemical nature (Prausnitz et al., 1999); 2- There are correlations regressed for TAGs allowing predicting the model parameters and 3- it allows flexibility/simplicity required in the optimization step. The necessary binary interaction parameters (A_{ij}) are calculated using correlations with the isomorphism in the pair of TAGs i - j (Wesdorp, 1990). The activity coefficients can be therefore estimated.

2.4. Pure Component Properties (Melting Temperature and Melting Enthalpy)

A program developed in FORTRAN 90 includes a set of 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 in all 3 polymorphic states. In these cases, the predictive methods of Zeberg-Mikkelsen and Stenby (1999) and Wesdorp (1990) are used.

2.5. Triacylglycerol Composition from Fatty Acids Data

The TAG composition is predicted from the known fatty acids data of each vegetable oil (Lida et al., 2002). Two TAG compositions are estimated: the TAG composition of the physical mixture of the oils and the TAG composition of the product of the chemical interesterification (CI) reaction among the oils. In the first case, the TAG composition of each oil is firstly estimated (by computational random distribution of fatty acids in the glycerol); then, a material balance gives the TAG composition of the mixture. In the second case, firstly 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 CI reaction. The CI is a technique to change melting profile of vegetable oils blends. This reaction promotes a random distribution of fatty acids among the 3 positions of glycerol.

3. Solution Approach

The optimization step (Eqs. (1-3)) was implemented in GAMS (v.23) 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, 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. The results from the optimization step are the number of mols of each TAG in each phase (solid and liquid). Thus, one can compute the solid/liquid ratio (SFC) given the temperature and fraction of each vegetable oil in the blend.

4. Case Study

The method was applied to a ternary system: palm oil (PO) – sunflower oil (SFO) – palmkernel oil (PKO) before and after CI reaction. An increment of 5 % in each vegetable oil is used to cover the ternary diagram. For a given temperature, 231 optimization problems are solved (57 binary, 3 pure vegetable oil and 171 ternary problems). The same diagram is evaluated before and after CI, therefore a total of 462 SLE problems are solved in a single temperature. Spanning the procedure to 8 temperatures, 3,696 SLE problems are solved. The results were compared with experimental SFC data from Lida et al. (2002). The number of experimental points is 256: 128 before CI (16 composition x 8 temperatures) and 128 after CI (16 compositions x 8 temperatures). Only 64 experimental points refer to ternary blends.

5. Results and Discussion

The average absolute error (AAE) in SFC is indicated in Table 1, covering the points with available experimental data. The predicted thermal profile covering the ternary diagram (231 SLE problems) with corresponding temperatures and computational times are shown for simple mixtures without reaction (Figure 2) and for interesterified blends (Figure 3). Analyzing the computational results over the 256 experimental values, different model performances arise. Points with very high agreement were found. For example, for the mixture (without reaction): pure PO at 25 °C (SFC experimental = 11.3; SFC calculated = 11.0); binary PO/SFO (50/50) at 20 °C (SFC experimental = 5.2; SFC calculated = 5.0); ternary PO/SFO/PKO (1/4/1) at 5 °C (SFC experimental = 9.8; SFC calculated = 12.0). The same occurs for interesterified blends: pure PKO at 15 °C (SFC experimental = 36.3; SFC calculated = 36.0); binary SFO/PKO (50/50) at 10 °C (SFC experimental = 6.2; SFC calculated = 6.0); ternary PO/SFO/PKO (4/1/1) at 30 °C (SFC experimental = 3.3; SFC calculated = 3.0). However, large deviations were also observed.

Table 1. Average absolute error of Solid Fat Content predictions.

| Mixture | 5 °C | 10 °C | 15 °C | 20 °C | 25 °C | 30 °C | 35 °C | 40 °C |
|--------------------------|------|-------|-------|-------|-------|-------|-------|-------|
| Single VO | 7.3 | 7.5 | 3.9 | 2.2 | 5.9 | 4.5 | 2.8 | 0.1 |
| Binary blends | 5.3 | 4.5 | 6.0 | 9.9 | 8.9 | 5.2 | 3.2 | 0.8 |
| Ternary blends | 3.7 | 5.7 | 9.9 | 12.2 | 9.1 | 6.1 | 3.5 | 0.5 |
| Chemical Reaction | | | | | | | | |
| Single VO | 10.1 | 5.9 | 3.3 | 7.2 | 7.3 | 5.6 | 1.8 | 0.1 |
| Binary blends | 11.5 | 8.1 | 4.7 | 2.9 | 2.3 | 1.2 | 0.2 | 0.4 |
| Ternary blends | 15.6 | 9.4 | 4.1 | 2.1 | 2.1 | 0.6 | 0.0 | 0.0 |

VO: vegetable oil

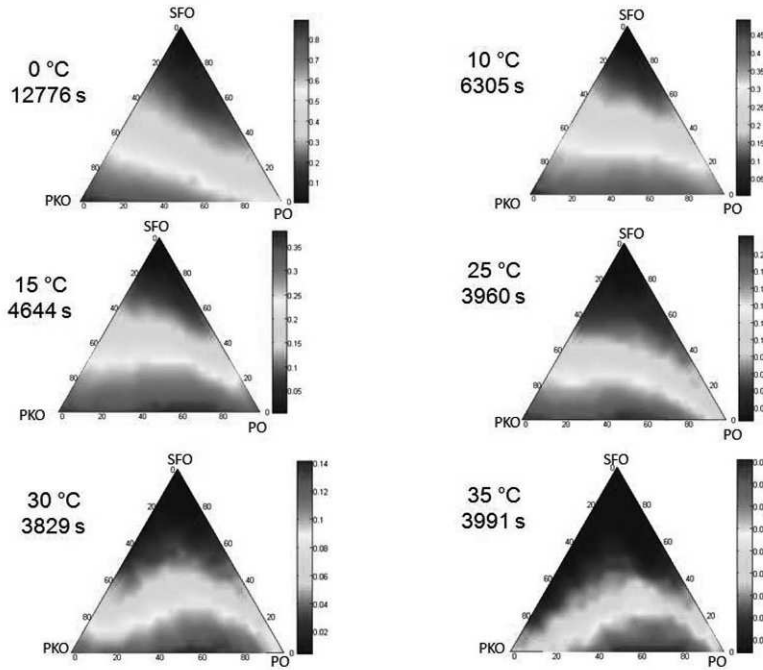


Figure 2. Predictions of Solid Fat Content for the system palm oil (PO) – sunflower oil (SFO) – palmkernel oil (PKO) without interesterification reaction.

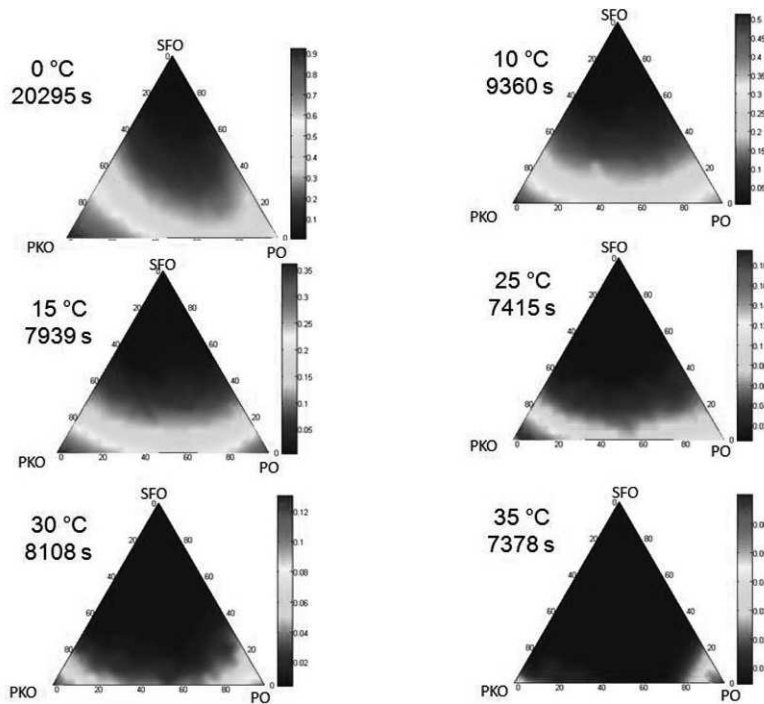


Figure 3. Predictions of Solid Fat Content for the system palm oil (PO) – sunflower oil (SFO) – palmkernel oil (PKO) with interesterification reaction.

For mixture: pure PO at 5 °C (SFC experimental = 63.1; SFC calculated = 42.0); binary PO/PKO (50/50) at 20 °C (SFC experimental = 7.5; SFC calculated = 31.0); ternary PO/SFO/PKO (1/1/4) at 20 °C (SFC experimental = 5.8; SFC calculated = 22.0). For systems after reaction: pure PO at 5 °C (SFC experimental = 62.2; SFC calculated = 42.0); binary PO/PKO (50/50) at 5 °C (SFC experimental = 55.0; SFC calculated = 34.0); ternary PO/SFO/PKO (4/1/1) at 5 °C (SFC experimental = 44.6; SFC calculated = 21.0). However, given the large number of SLE problems solved, the average values (Table 1) and the large combinatorial space in product formulation, the agreement between calculated and experimental data is within an acceptable tolerance. From Figures 2 and 3, it can be noted a sharp reduction in SFC after CI reaction. This is due to the reduction in the content of saturated TAGs (higher melting point). The CI reaction causes a random 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.

6. Conclusions

Computer-aided tools are useful to observe the influence of the fraction of each vegetable oil, temperature and interesterification reaction in vegetable oils blends. When compared to experimental SFC, the model showed a similar performance with pure vegetable oils and binary blends (AAE = 4.7) and a slightly decrease in performance with ternary blends (AAE = 5.3). The main model limitations concern pure component property predictions, deviations of real systems from the simplification hypotheses of random distribution of fatty acids and limitations from the Excess Gibbs energy model.

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