Modelling of the phase behaviour for vegetable oils at supercritical conditions

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ABSTRACT

This work describes a generalized procedure for high pressure equilibrium calculations for vegetable oils. The present approach considers any vegetable oil as composed by two key components: oleic acid (OA) and triolein (TO). OA is representing the low molecular weight compounds, those related with acid value and the products of degradation. TO refers the fatty content. The mathematical procedure used commercial ASPEN-plus® software package to process CO_2–OA–TO equilibrium data according to the classical cubic equations of state (EOS). The theoretical data calculated by the package fit fairly well with the experimental results published for a wide variety of vegetable oils, especially for seed extracts. Equilibrium calculation theoretical results were in good agreement with literature data for acid value and also confirmed than can be used to predict properly continuous countercurrent processes.

The model proposed in this work can be useful for preliminary scale-up and economical evaluations avoiding specific equilibrium data determination, with special interest in deacidification processes.

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1. Introduction

Vegetable oils represent an important market in the world with a wide variety of economical areas of interest, from human or animal nutrition to biochemical or bioenergy production. Vegetable oils are usually recovered from natural matrixes by pressing and/or solvent extraction procedures. Crude vegetable oils are submitted to refining processes for purification and to avoid degradation reactions. In the case of human consumption, this procedure is especially complex in order to follow the strict food normative regulations [1].

SFE has been demonstrated as a technically viable alternative to both, extraction and refining processes. Their high selectivity leads to obtain, in single step or sequential extractions, commercial oil fractions with all quality parameters according to food normative [2,3]. In spite of the large variety of applications proposed in literature, pilot scale or industrial applications for vegetable oils extraction are limited. The only economically feasible SFE application to vegetable oils would involve the isolation of high valuable compounds or using high-scale continuous countercurrent operation [4]. The lack of equilibrium data about extraction and fractionation, in addition to the complexity of thermodynamic models make difficult to obtain generic equilibrium predictions for multicomponent mixtures. These predictions would provide necessary information in preliminary scale-up economical evaluations.

del Valle and Aguilera [5] proposed a simple correlation to predict vegetable oil solubility in CO_2 that considered any vegetable oil like a single component, without providing information about equilibrium composition. In spite of their great deviations, its wide applicability promoted as the reference equation for vegetable oil solubility estimation in process design, kinetics and equilibrium calculations. The few attempts in multicomponent mixtures modelling to represent vegetable oils involved complex computing and low applicability to oils different than those studied [4].

The aim of this work is to propose an approach to describe any vegetable oil like a mixture of key components. Considering this assumption and using the literature equilibrium data for the selected key components, this work develops a procedure using ASPEN-plus® software package to estimate vegetable oils equilibrium data in supercritical CO_2. Validity of estimations will be checked by comparing both, solubility and fractionation data for a wide variety of vegetable oils described in literature.

2. Procedure

2.1. Thermodynamic model

In this work the Peng–Robinson–Boston–Mathias (PR-BM) and Redlich–Kwong–Soave (RKS) equations of state are used as was included in Aspen software package. Table 1 shows the set of equations of both equations of state (EOS) [6–11].

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Table 1
RKS and PR-BM EOS's and mixing rules.

EOS considered in this work	RKS with Aspen mixing rules (RKS–Aspen) EOS	Peng–Robinson–Boston–Mathias (PR-BM) EOS
Standard EOS	$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b)}$ where $$b = \sum_i x_i b_i = 0.08664 RT_{c_i}/P_{c_i}$$ $$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij}) = 0.42747\alpha_i R^2 T_{c_i}^2 / P_{c_i}$$ $k_{ij} = k_{ji}$ $\alpha_i = \left[1 + m_i(1 - T_{r_i}^{1/2})\right]^2$ $m_i = 0.48 + 1.57\omega_i - 0,176\omega_i^2$	$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}$ where $$b = \sum_i x_i b_i$$ $$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{ij})$$ $b_i = f(T_{ci}, P_{ci}) = 0.07780\frac{RT_{c_i}}{P_{c_i}}$ $a_i = f(T, T_{c_i}, P_{c_i}, \omega_i) = 0.45724\alpha_i \frac{R^2 T_{c_i}^2}{P_{c_i}}$ $k_{ij} = k_{ji}$
Modification	RKS with Aspen mixing rules $$b = \sum_i \sum_j x_i x_j \frac{b_i b_j}{2}(1 - k_{b,ij})$$ $$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5}(1 - k_{a,ij})$$ $b_i = f(T_{ci}, P_{ci})$ $a_i = f(T, T_{c_i}, P_{c_i}, \omega_i, \eta_i)$ $k_{a,ij} = k_{a,ij}^0 + k_{a,ij}^1 T/1000$ $k_{b,ij} = k_{b,ij}^0 + k_{b,ij}^1 T/1000$	In Boston–Matias modification of PR EOS $\alpha_i = [\exp[c_i(1 - T_{r_i}^{d_i})]]^2$ with $d_i = \left(1 + \frac{m_i}{2}\right)$ $c_i = 1 - \frac{1}{d_i}$ $m_i = 0.3764 + 1.54226\omega_i - 0.26992\omega_i^2$

For details see references [6–11].

2.2. Development of a hypothesis to describe vegetable oils

Vegetable oils are mixtures of glycerides, fatty acids and minor compounds like hydrocarbons, alcohols, phenols, tocopherols, phospholipids, chlorophylls and waxes [1]. Our approach considers that a vegetable oil is formed by two key components representing the most abundant group of compounds: triglycerides and free fatty acids. Triglycerides refer the fatty oil content, while the free fatty acids, produced by their hydrolysis give information about oil degradation. This content is used to establish the quality oil rankings, expressed in terms of acid value parameter.

Taking into account that the solubility differences between particular components of any family are small compared to the corresponding values between global families [12], we have selected one particular compound from each family: triolein (TO) for triglycerides and oleic acid (OA) for free fatty acids, given that oleic acid is the reference component to express acid value.

2.3. Equilibrium predictions: solubility and fractionation calculations

Equilibrium calculations were performed according to the procedure resumed in Fig. 1. Commercial ASPEN-plus® software package was used to process ternary and pseudo binary CO_2–OA–TO
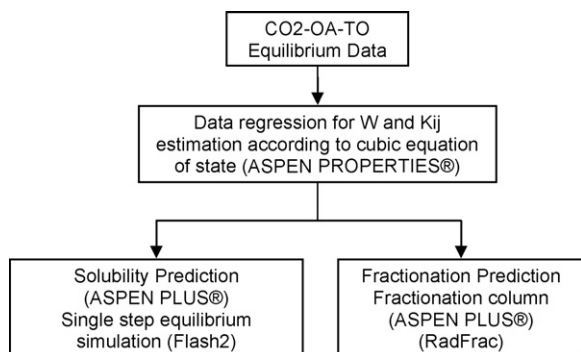
equilibrium data from Bharath et al. [13] according to RKS and PR-BM cubic equations of state to obtain acentric factors, ω, and binary interaction parameters, k_{ij}. We used critical parameters for the pure compounds from the Aspen Properties 1.11 database and the feed OA value (in the 0–30% range) that gives minimum deviations considering that in most cases this information is unknown. We discarded OA values over 30% because they are not usual and to avoid the use of OA as a free fit parameter.

Validity of predictions was checked by comparing bibliographic information about oleic acid, triolein and vegetable oil solubility in CO_2 in addition to data about fractionation of oil components. For the first comparison it was used single step equilibrium simulation. In this case, our results for the global solubility were obtained by the addition of AO and TO equilibrium results. Literature data about fractionation was compared using the predictions corresponding to a distillation column.

3. Results and discussion

According to the procedure described in Fig. 1 the Bharath et al. [13] equilibrium data obtained in pressure (P) and temperature (T) ranges of 20–30 MPa and 313.15–333.15 K were processed to obtain the parameters of the EOS's shown in Table 2. This information was used for the ulterior equilibrium predictions in the same P/T intervals. As observed in Fig. 2 for PR-BM EOS at 313.15 K and pressure ranging from 20 to 30 MPa, the equilibrium predictions (open symbols) were in good agreement with experimental data (solid symbols). Considering the acceptable deviations and simplicity (six k_{ij} parameters), PR-BM was selected to do the rest of equilibrium estimations.

3.1. Solubility

3.1.1. Theoretical predictions

The model predictions were studied by varying the relations: CO_2/oil and OA/oil mass fractions. CO_2/oil represents the solvent to feed ratio, while as OA/oil is the acid value of feed oil. Both parameters are well defined in most of industrial processes. Fig. 3 shows the predicted solubility (OA + TG) as a function of acid value and

Fig. 1. Process scheme to obtain multicomponent equilibrium data.