

Article

Simulation of organic liquid products deoxygenation by multistage countercurrent absorber/stripping using CO₂ as solvent with Aspen-Hysys: Thermodynamic data basis and EOS modeling

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Abstract: In this work, the thermodynamic data basis and EOS modeling necessary to simulate the fractionation of organic liquid products (OLP), a liquid reaction product obtained by thermal catalytic cracking of palm oil at 450°C, 1.0 atmosphere, with 10% (wt.) Na₂CO₃ as catalyst, in multi-stage countercurrent absorber/stripping columns using SC-CO₂ as solvent, with Aspen-Hysys was systematically investigated. The chemical composition of OLP was used to predict the physical (ρ), thermo-physical properties (T_b , T_c , P_c , V_c), and acentric factor (ω) of all the compounds present in OLP by applying the group contribution methods of Marrero-Gani, Han-Peng, Marrero-Pardillo, Constantinou-Gani, Joback and Reid, and Vetere. The RK-Aspen (EOS) used as thermodynamic fluid package, applied to correlate the experimental phase equilibrium data of binary systems organic liquid products compounds (OLP)-i/CO₂ available in the literature. The group contribution methods selected based on the lowest relative average deviation by computing T_b , T_c , P_c , V_c , and ω . For n-alkanes, the method of Marrero-Gani selected for the prediction of T_c , P_c and V_c , and that of Han-Peng for ω . For alkenes, the method of Marrero-Gani selected for the prediction of T_b and T_c , Marrero-Pardillo for P_c and V_c , and Han-Peng for ω . For unsubstituted cyclic hydrocarbons, the method of Constantinou-Gani selected for the prediction of T_b , Marrero-Gani for T_c , Joback for P_c and V_c , and the undirected method of Vetere for ω . For substituted cyclic hydrocarbons, the method of Constantinou-Gani selected for the prediction of T_b and T_c , Marrero-Gani for T_c and V_c , and the undirected method of Vetere for ω . For aromatic hydrocarbon, the method of Joback selected for the prediction of T_b , Constantinou-Gani for T_c and V_c , Marrero-Gani for P_c , and the undirected method of Vetere for ω . The regressions show that RK-Aspen EOS was able to describe the experimental phase equilibrium data for all the binary pairs undecane-CO₂, tetradecane-CO₂, pentadecane-CO₂, hexadecane-CO₂, octadecane-CO₂, palmitic acid-CO₂, and oleic acid-CO₂, showing average absolute deviation (AAD_x) between 0.8% and 1.25% for the liquid phase and (AAD_y) between 0.01% to 0.66% for gaseous phase.

Keywords: OLP; Thermodynamic Data Basis; EOS Modeling; Process Simulation; Aspen-Hysys.

1. Introduction

The liquid reaction products (OLP) of thermal catalytic cracking of lipid-base materials, including vegetable oils [1-17], residual oils [18-25], animal fats [26-28], residual animal fat [27], mixtures of carboxylic acids [28-33], soaps of carboxylic acids [34-35], and scum, grease & fats [36-38], may be used as liquid fuels [1-2, 4-8, 10-11, 13-19, 20, 22, 26,

35-41], if proper upgrading processes (distillation, adsorption, and liquid-liquid extraction) are applied to remove the oxygenates [6-7, 10, 16-19, 35-41]. In order to be used as a liquid fuel, the upgraded and/or de-acidified OLP, must also match the most important physicochemical (acid value, flash point, carbon residue, cloud point, water in sediments, copper corrosiveness), physical (density), and transport properties (kinematic viscosity) to fossil-fuel specifications [10, 16-19, 35-41].

The organic liquid products (OLP) are composed by alkanes, alkenes, ring-containing alkanes, ring-containing alkenes, cyclo-alkanes, cyclo-alkenes, and aromatics [4, 8, 10, 16-19, 26, 28-29, 34-38], as well as oxygenates including carboxylic acids, aldehydes, ketones, fatty alcohols, and esters [4, 6-8, 10, 16-17, 26, 28, 34-41].

A process with great potential to remove and/or recover oxygenates from OLP (De-acidification of OLP) is multistage gas extraction, using SC-CO₂ as solvent, based on similar studies reported in the literature [42-43]. However, knowledge of phase equilibrium for the complex system OLP/CO₂ is necessary.

The knowledge of phase equilibrium data is of fundamental importance for the design of equilibrium-stage separation processes (e.g. multistage gas extraction, absorption, liquid-liquid extraction, distillation), as it provides the thermodynamic basis for the separation process analysis [44].

High pressure phase equilibrium data yields information concerning the solubility of the coexisting gas-liquid phases, solvent capacity, compositions of the coexisting phases, distribution coefficients, and selectivity [44]. Those measurements are time consuming, needs special infrastructure (equilibrium cells, sampling units, and compressors), sophisticated chemical analysis (GC-MS, HPLC, etc.), and qualified human resources, thus posing not only a complex experimental task, but also high investment and operational costs [44-45].

In this context, *the construction of a thermodynamic data basis is necessary for the modeling of complex/multi-component mixtures/CO₂ using EOS*. Process thermodynamic modeling of complex mixtures/CO₂ using EOS, is a powerful tool to provide preliminary information of high-pressure phase equilibrium of complex multi-component systems/CO₂, for guiding experimental high-pressure phase equilibrium measurements, as well as to reduce the number of necessary experiments, but not to replace experimental data [45].

Modern design of equilibrium stage processes (e.g. fractionation of multi-component liquid mixtures by multistage countercurrent absorber/stripping columns using supercritical CO₂ as solvent) requires thermodynamic models capable of predicting the chemical composition of the coexisting phases without the preliminary use of experimental data. In addition, the applied thermodynamic models must be capable to perform accurate computation of mutual solubility's of the coexisting liquid and gaseous phases in both sub-critical and critical regions [46]. However, simultaneous fulfillment of these requirements is a very difficult and challenging task for EOS [47-48].

The inaccuracy of EOS to predict the chemical composition and the mutual solubility's of the coexisting phases in both the sub-critical and critical regions for complex systems/CO₂, may be overcome if phase equilibrium data for some of the binary pairs (multi-component mixture compounds)-i/CO₂ are available in the literature [46].

A key point in this approach is to determine the binary interaction parameters binary k_{aij} and k_{bij} by correlating phase equilibrium data for the binary pairs (multi-component mixture compounds)-i/CO₂ available in the literature [46]. Knowledge of binary interaction parameters makes it possible to construct the matrix of binary interaction parameters [46].

The RK-Aspen EOS with the van der Waals mixing rules and RK-Aspen combining rules for two temperature-independent binary interaction parameters $k_{aij} = k_{aij}^0$ and $k_{bij} = k_{bij}^0$, and the k_{ij} between two components i and j is a function of the pure component critical properties (T_{ci} , T_{cj} , P_{ci} , P_{cj}) and acentric factors (ω_i , ω_j). In this sense, it is necessary to compute the critical properties and acentric factors of all the chemical species present in the composition of complex/multi-component mixture [46].

EOS of van der Waals type with van der Waals quadratic mixing rules, including the PR-EOS with van der Waals quadratic mixing rules, PR-EOS with quadratic mixing rules, PR-EOS with a temperature dependent binary interaction parameter k_{ij} , computed by a group contribution method, applied to predict high-pressure phase equilibrium for the binary systems carboxylic acids-CO₂, hydrocarbons-CO₂, and fat-soluble substances-CO₂ [45-55]. Most studies analyzed the thermodynamic modeling of binary systems carboxylic acids-CO₂, alkanes-CO₂, alkenes-CO₂, cycloalkanes-CO₂, cycloalkenes-CO₂, aromatics-CO₂, alcohols-CO₂, fat-soluble substances-CO₂, and fatty alcohols-CO₂ [45-55], representing the majority of the binary pairs OLP-*i*/CO₂, but also complex multi-component systems/CO₂ [45-46]. In addition, group contribution (GC) method combined with the perturbed-chain SAFT (PC-SAFT) and variable-range SAFT (VR-SAFT) EOS, applied to predict high-pressure phase equilibrium for the binary systems *n*-alkanes/CO₂ [56].

Modeling of high-pressure phase equilibrium includes the application of PR-EOS with van der Waals quadratic mixing rules for the binary systems pentane-CO₂ and toluene-CO₂ [49], PR-EOS with van der Waals quadratic mixing rules for the binary systems palmitic acid-CO₂, oleic acid-CO₂, linoleic acid-CO₂, stigmaterol-CO₂, α -tocopherol-CO₂, squalene-CO₂, and the complex multi-component system Soy Oil Deodorizer Distillates (SODD)-SC-CO₂, lumped as a mixture of key compounds palmitic acid, oleic acid, linoleic acid, stigmaterol, α -tocopherol, and squalene [45], PR-EOS with quadratic mixing rules for the binary systems toluene-CO₂, benzene-CO₂, and *n*-hexane-CO₂ [50], PR-EOS with a group contribution method to estimate the binary interaction parameters k_{ij} for 54 (fifty four) binary systems hydrocarbons-CO₂ [47], PPR78 EOS with temperature dependent k_{ij} calculated using group contribution method to systems containing aromatic compounds-CO₂ [48], cubic EOS (PR, 3P1T, and PR-DVT), and EOS with association term (PR-CPA EOS, AEOS, SAFT, and SAFT-CB) for the binary systems *o*-cresol-CO₂, *p*-cresol-CO₂, and ternary system *o*-cresol-*p*-cresol-CO₂ [51], SRK EOS with association model to correlate the solubility's of fatty acids (myristic acid, palmitic acid and stearic acid) and fatty alcohols (1-hexadecanol, 1-octadecanol, and 1-eicosanol in SC-CO₂ [52], RK-Aspen and PR-BM EOS for the binary systems oleic acid-CO₂, triolein-CO₂, using the ASPEN-plus® software to predict high-pressure phase equilibrium of multicomponent mixture vegetable oil-CO₂, lumped as a mixture of key compounds oleic acid and triolein, thus represented by the ternary system oleic acid-triolein-CO₂ [53], RK-Aspen, PR-BM and SR-POLAR EOS for the binary systems *n*-dodecane-CO₂, 1-decanol-CO₂, and 3,7-dimethyl-1-octanol-CO₂, for the ternary system *n*-dodecane-1-decanol-CO₂, *n*-dodecane-3,7-dimethyl-1-octanol-CO₂, 3,7-dimethyl-1-octanol-1-decanol-CO₂, and the quaternary system *n*-dodecane-3,7-dimethyl-1-octanol-1-decanol-CO₂, using the ASPEN-plus® software to predict high-pressure phase equilibrium of multi-component mixture *n*-dodecane-3,7-dimethyl-1-octanol-1-decanol-CO₂ [54], PPC-SAFT EOS to predict the global behavior of the binary pair *n*-alkanes-CO₂ [55], GC-SAFT EOS (Perturbed-Chain SAFT and Variable-Range SAFT) for the binary systems *n*-alkanes-CO₂, including propane-CO₂, *n*-butane-CO₂, *n*-pentane-CO₂, *n*-hexane-CO₂, *n*-heptane-CO₂, *n*-octane-CO₂, *n*-decane-CO₂, *n*-dodecane-CO₂, *n*-tetradecane-CO₂, *n*-eicosane-CO₂, *n*-docosane/CO₂, *n*-octacosane/CO₂, *n*-dotriacontane/CO₂, *n*-hexatriacontane/CO₂, and *n*-tetratriacontane-CO₂ [56], RK-Aspen for the binary systems organic liquid products compounds-*i*-CO₂, including undecane-CO₂, tetradecane-CO₂, pentadecane-CO₂, hexadecane-CO₂, octadecane-CO₂, palmitic acid-CO₂, and oleic acid-CO₂, using the Aspen-Hysys software to predict high-pressure phase equilibrium of multi-component system PLO-SC-CO₂ [46].

In this work, the thermodynamic data basis and EOS modeling necessary to simulate the fractionation of OLP in multistage countercurrent absorber/stripping columns using SC-CO₂ as solvent, with Aspen-Hysys was systematically constructed. The physical (ρ), critical properties (T_b , T_c , P_c , V_c), and acentric factor (ω) of all the compounds present in OLP predicted by the group contribution methods of Marrero-Gani, Han-Peng, Marrero-Pardillo, Constantinou-Gani, Joback and Reid, and Vetere. The RK-Aspen applied to correlate the experimental phase equilibrium data of binary systems organic liquid products compounds (OLP)-*i*-CO₂ available in the literature. The regressions show that RK-Aspen EOS was able

to describe the experimental phase equilibrium data for all the binary pairs (multi-component mixture compounds)-i-CO₂ under investigation.

2. Modeling and simulation methodology

2.1. Thermodynamic modeling

2.1.1. Prediction of thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of OLP compounds

Predictive methods selected by considering their applicability to describe the chemical structure of molecules, including the effects of carboxylic acids and hydrocarbons chain length and molecular weight, and simplicity of use.

Experimental data of normal boiling temperature (T_b) and critical properties (T_c , P_c , V_c) of carboxylic acids [57-58], esters of carboxylic acids [57-58], hydrocarbons [59-60], and alcohols [58-61], reported by Ambrose and Ghiasse [57], Simmrock *et al.* [58], Danner and Daubert [59], Yaws [60], and Teja *et al.* [61], as well as vapor pressure (P^{Sat}) data reported by Ambrose and Ghiasse [57], and Boublik *et al.* [62], used to evaluate all the methods applied to predict the thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of OLP compounds described in Table 1.

Based on the chemical composition of OLP described in Table 1, experimental data for critical properties available in the literature selected to the following class of hydrocarbons including alkanes from C₂-C₂₀, cyclic from C₃-C₁₇, alkenes with only one double bound from C₄-C₂₀, and aromatics from C₆-C₁₅, carboxylic acids of linear chain length from C₁-C₁₀, as well as C₁₆, C₁₈, C₂₀, and C₂₂, carboxylic acids with one or two double bounds including C_{16:1}, C_{16:2}, C_{18:1}, C_{18:2}, C_{20:1}, C_{20:2}, C_{22:1}, C_{22:2}, alcohols of linear chain length from C₂-C₁₀.

Table 1. Chemical composition of OLP, obtained by thermal catalytic cracking of palm oil at 450 °C, 1.0 atmosphere, with 10% (wt.) Na₂CO₃ [17], used to predict the thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of all the compounds present in OLP.

Chemical Compounds	Molecular Formula	CAS Number
Metil-Cyclooctane	C ₉ H ₁₈	1502-38-1
1-Butyl-1-Cyclohexene	C ₁₀ H ₁₈	3282-53-9
3-Isobutyl-1-Cyclohexene	C ₁₀ H ₁₈	4104-56-7
1-Decene	C ₁₀ H ₂₀	872-5-9
Decane	C ₁₀ H ₂₂	124-18-5
1-Hexil-Cyclopentene	C ₁₁ H ₂₀	Not Available
1-Undecene	C ₁₁ H ₂₂	821-95-4
(E)-2-Undecene	C ₁₁ H ₂₂	693-61-8
(Z)-2-Undecene	C ₁₁ H ₂₂	Not Available
Undecane	C ₁₁ H ₂₄	1120-21-4
1-Dodecene	C ₁₂ H ₂₄	112-41-4
1-Tridecene	C ₁₃ H ₂₆	2437-56-1
Cyclotridecane	C ₁₃ H ₂₆	295-02-3
Tridecane	C ₁₃ H ₂₈	629-50-5
1-Octyl-Cyclohexene	C ₁₄ H ₂₆	15232-87-8
1-Tetradecene	C ₁₄ H ₂₈	1120-36-1
Cyclotetradecane	C ₁₄ H ₂₈	295-17-0
Tetradecane	C ₁₄ H ₃₀	629-59-4
1-Nonyl-1-Cyclohexene	C ₁₅ H ₂₈	15232-88-9

1-Pentadecene	C ₁₅ H ₃₀	13360-61-7
Nonylcyclohexane	C ₁₅ H ₃₀	2883-02-5
Cyclopentadecane	C ₁₅ H ₃₀	295-48-7
Pentadecane	C ₁₅ H ₃₂	629-62-9
(Z)-7-Hexadecene	C ₁₆ H ₃₂	Not Available
(Z)-3-Hexadecene	C ₁₆ H ₃₂	34303-81-6
1-Hexadecene	C ₁₆ H ₃₂	629-73-2
Cyclohexadecane	C ₁₆ H ₃₂	295-65-8
Hexadecane	C ₁₆ H ₃₄	544-76-3
1-Heptadecene	C ₁₇ H ₃₄	6765-39-5
(E)-9-Octadecene	C ₁₈ H ₃₆	5557-31-3
Octadecane	C ₁₈ H ₃₈	593-45-3
(E)-9-Eicosene	C ₂₀ H ₄₀	Not Available
(Z)-9-Tricosene	C ₂₃ H ₄₆	27519-2-4
Caproic Acid	C ₆ H ₁₂ O ₂	142-62-1
Glycerol	C ₃ H ₈ O ₃	56-81-5
N-Nonanoic Acid	C ₉ H ₁₈ O ₂	112-05-0
Capric Acid	C ₁₀ H ₂₀ O ₂	334-48-5
Lauric Acid	C ₁₂ H ₂₄ O ₂	143-07-7
Myristic Acid	C ₁₄ H ₂₈ O ₂	544-63-8
2-Nonadecanone	C ₁₉ H ₃₈ O	629-66-3
Ethyl Palmitate	C ₁₈ H ₃₆ O ₂	628-97-7
Octadecan-4-one	C ₁₈ H ₃₆ O	Not Available
Palmitic Acid	C ₁₆ H ₃₂ O ₂	57-10-3
Z-10-Octadecene-1-ol Acetate	C ₂₀ H ₃₈ O ₂	Not Available
1-Eicosanol	C ₂₀ H ₄₂ O	629-96-9
Ethyl Oleate	C ₂₀ H ₃₈ O ₂	111-62-6
Linoleic Acid	C ₁₈ H ₃₂ O ₂	60-33-3
Oleic Acid	C ₁₈ H ₃₆ O	112-80-1
Stearic Acid	C ₁₈ H ₃₆ O ₂	57-11-4
8-Octadecanone	C ₁₈ H ₃₆ O	79246-41-6

2.1.1.1. Methods to predict thermo-physical (T_b) and critical properties (T_c, P_c, V_c)

The predictive methods by Joback and Reid [63], Constantinou-Gani [64], Marrero-Marejón and Pardillo-Fontdevila [65], and Marrero-Gani [66] applied to estimate the normal boiling temperature (T_b) and critical properties (T_c, P_c, V_c) of all the compounds present in OLP. Table 2 presents the equations of all the predictive methods applied to compute T_b, T_c, P_c, and V_c [63-66].

The method by Constantinou-Gani [64], is based only on the molecular structure of molecules, being applied in two levels: the first level treats simple functional groups, also called first order groups, and the second level treats the second order groups, formed by blocks of first order groups. In the equations described in Table 2, T_{b1i}, T_{c1i}, P_{c1i} and V_{c1i}, represent the group contribution of first order level for the corresponding properties, and N_i how many times the group i occurs in the molecule. In a similar way, T_{b2j}, T_{c2j}, P_{c2j} and V_{c2j} represents the group contributions of second order level, and M_j how many times the group j occurs in the molecule.

Marrero-Gani [66], proposed a method analogous to that of Constantinou-Gani [64], in which a group contribution of third order is added, whereas T_{b3k} , T_{c3k} , P_{c3k} and V_{c3k} represent these contributions, and O_k how many times the group k occurs in the molecule.

Table 2. The equations used to predict/estimate the thermo-physical (T_b) and critical properties (T_c , P_c , V_c) of all the compounds present in OLP, by the methods of Joback and Reid [63], Constantinou and Gani [64], Marrero-Marejón and Pardillo-Fontdevila [65] and Marrero and Gani [66].

Constantinou-Gani [64]	Marrero-Gani [66]
$T_b = 204.359 \ln \left(\sum_i N_i(T_{b1i}) + W \sum_j M_j(T_{b2j}) \right)$	$T_b = 222.543 \ln \left(\sum_i N_i T_{b1i} + \sum_j M_j T_{b2j} + \sum_k O_k T_{b3k} \right)$
$T_c = 181.128 \ln \left(\sum_i N_i T_{c1i} + W \sum_j M_j T_{c2j} \right)$	$T_c = 231.239 \ln \left(\sum_i N_i T_{c1i} + \sum_j M_j T_{c2j} + \sum_k O_k T_{c3k} \right)$
$(P_c - 1.3705)^{-0.5} - 0.10022$ $= \sum_i N_i p_{c1i} + \sum_j M_j p_{c2j}$	$(P_c - 5.9827)^{-0.5} - 0.108998$ $= \sum_i N_i P_{c1i} + \sum_j M_j P_{c2j} + \sum_k O_k P_{c3k}$
$V_c + 0.00435 = \sum_i N_i v_{c1i} + \sum_j M_j v_{c2j}$	$V_c - 7.95 = \sum_i N_i V_{c1i} + \sum_j M_j V_{c2j} + \sum_k O_k V_{c3k}$
Joback & Reid [63]	Marrero-Pardillo [65]
$T_b = 198.2 + \sum n_i T_{bi}$	$T_b = 204.66 + \Sigma$
$T_c = T_b \left[0.584 + 0.965 \left(\sum n_i T_{ci} \right) - \left(\sum n_j T_{cj} \right)^2 \right]^{-1}$	$T_c = T_b / [0.5851 - 0.9286 \Sigma - \Sigma^2]$
$P_c = \left(0.113 + 0.0032 n_A - \sum n_i P_{ci} \right)^{-2}$	$P_c = (0.1285 - 0.0059 n_A - \Sigma)^{-2}$
$V_c = 17.5 + \Sigma$	$V_c = 25.1 + \Sigma$

Joback and Reid [63], proposed a method to estimate the normal boiling temperature (T_b) and critical properties (T_c , P_c , V_c) using group contribution, where Σ symbolizes the sum of all the contributions of each group corresponding to the parts of a molecule. To compute the critical temperature (T_c), Joback and Reid [63] proposed a method dependent on the normal boiling temperature (T_b).

By the method of Joback and Reid [63], n_i is the number of contributions, while T_{bi} and T_{ci} are the normal boiling temperature and critical temperature associated to the i -th group contribution. To compute the critical pressure (P_c), the method by Joback and Reid [63], considers the number of atoms within the molecule, where n_A specifies the number of atoms in the molecule, and P_{ci} the critical pressure associated to the i -th group contribution.

Marrero-Pardillo [65], proposed a method to predict the normal boiling temperature (T_b) and critical properties (T_c , P_c , V_c) of pure organic molecules that uses a novel structural approach. This methodology uses the interactions between the groups of charges within the molecule, instead of the simple group contribution. To estimate the critical pressure (P_c), and likewise the method by Joback and Reid [63], this method also considers the number of atoms in the molecule.

2.1.1.2. Methods selected to predict the acentric factor (ω)

The prediction of acentric factor performed by using direct group contribution methods as described by Constantinou *et al.* [67] and Han and Peng [68], as well as an indirect

method using its definition from vapor pressure data, based on the proposal of Araújo and Meireles [69]. In this case, the correlation by Vetere [70] was used, making it possible to estimate the vapor pressure from molecular structure. Experimental values for acentric factors obtained as the follows:

- I. Predicted by using experimental data of critical properties, and experimental data of vapor pressure at $T_r = 0.7$ [71];
- II. Predicted by using experimental values of critical properties and vapor pressure data at $T_r = 0.7$, computed with Wagner's equation [72], and the parameters obtained from experimental data fitting.

2.1.2. Statistical analysis of predicted thermo-physical property (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of OLP compounds

The same criteria used by Melo *et al.* [73] and Araújo and Meireles [69] were used to select the best methods to predict the thermo-physical property, critical properties, and acentric factor of OLP compounds. The criteria based on statistical analysis (measurements of central tendency and dispersion).

The decisive criteria to select the best prediction methods for the thermo-physical properties, critical properties, and acentric factor are the measurement of central tendency, represented by the average relative deviation (ARD), the dispersion of deviations (R), and the standard deviation (S), using the procedures as follows:

- 1. The lower values for the average percent deviation (ARD) and standard deviation (S) define the best methods;
- 2. In cases where the lower average deviation corresponds to the higher standard deviation, or vice versa, the method is selected by the lower range of deviation (R).

The predicted data for the thermo-physical property, critical properties, and acentric factor computed by the methods and procedures described in sections 2.1.1.1 and 2.1.1.2, analyzed on basis its consistency related the physicochemical behavior expected for homologous series.

This test applied to hydrocarbons [74], by relating the thermo-physical property, critical properties, and the acentric factor with the number of carbons in carbon chain length or molecular weight of hydrocarbons.

2.1.3. Correlation of phase equilibrium data for the binary system OLP compounds-i-CO₂

2.1.3.1. EOS modeling

The thermodynamic modeling applied to describe the organic liquid products (OLP) fractionation in a multistage countercurrent absorber/stripping column using supercritical carbon dioxide (SC-CO₂) as solvent, performed by the Redlich-Kwong Aspen equation of state.

The RK-Aspen EOS equation of state applied to correlate the binary systems organic liquid products compounds-i-CO₂ available in the literature, as described in Table 3. The RK-Aspen EOS with the van der Waals mixing rules and RK-Aspen combining rules for two temperature-independent binary interaction parameters, described in details by Table 3.

Table 3. The RK-Aspen EOS with the van der Waals mixing rules and RK-Aspen combining rules for two temperature-independent binary interaction parameters $k_{aij} = k_{aij}^0$ and $k_{bij} = k_{bij}^0$.

Equation of state			
RK-Aspen	$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}$	$a = 0.42748 \frac{R^2 T_c^2}{P_c} \times \alpha(m_i, \eta_i, T_{ri})$	$b = 0.08664 \frac{RT_c}{P_c}$
		$\alpha(m_i, \eta_i, T_{ri}) = [1 + m_i(1 - T_{ri}^{1/2}) - \eta_i(1 - T_{ri})(0.7 - T_{ri})]^2$	

Mixing rules

$$\begin{aligned}
 a &= \sum_i \sum_j x_i x_j a_{ij} \\
 \text{van der Waals(RK-Aspen)} \quad b &= \sum_i \sum_j x_i x_j b_{ij} \\
 a_{ij} &= (a_{ii} a_{jj})^{1/2} (1 - k_{aij}) & k_{aij} &= k_{aij}^0 + k_{aij}^1 \frac{T}{1000} \\
 b_{ij} &= \frac{(b_{ii} b_{jj})}{2} (1 - k_{bij}) & k_{bij} &= k_{bij}^0 + k_{bij}^1 \frac{T}{1000}
 \end{aligned}$$

Where $k_{aij} = k_{aij}^0$ and $k_{bij} = k_{bij}^0$ are the binary interaction parameters, considered as temperature-independent. The RK-Aspen binary interaction parameters obtained using the Aspen Properties computational package from Aspen Plus. The program uses the Britt-Lueck algorithm, with the Deming parameters initialization method, to perform a maximum like-hood estimation of the following objective function, described by equation (1).

$$OF = \sum_i \left(\frac{T^e - T^c}{\sigma_T} \right)^2 + \sum_i \left(\frac{P^e - P^c}{\sigma_P} \right)^2 + \sum_i \left(\frac{x_i^e - x_i^c}{\sigma_x} \right)^2 + \sum_i \left(\frac{y_i^e - y_i^c}{\sigma_y} \right)^2 \quad (1)$$

Where, x_i^e and y_i^e are the experimental compositions of i-th compound in the coexisting liquid and gaseous phases, respectively, and σ the standard deviations, applied to the state conditions (T, P) and x_i^c and y_i^c compositions of i-th compound predicted with EOS. The average absolute deviation (AAD) computed to evaluate the agreement between measured experimental data and the calculated/predicted results for all the binary systems investigated.

2.1.3.2. High-pressure equilibrium data for the binary systems OLP compound-i-CO₂

Table 4 shows the experimental high-pressure gaseous-liquid equilibrium data for the binary systems OLP compound-i-CO₂ used to compute the binary interaction parameters. For the binary pairs OLP compounds-i-CO₂ not available in the literature, $k_{aij} = k_{aij}^0$ and $k_{bij} = k_{bij}^0$ were set equal to zero in the matrix of binary interaction parameters.

Table 4. Experimental gaseous-liquid equilibrium data for the binary pair's organic liquid products compounds-i-CO₂ used to compute the binary interaction parameters of RK-Aspen equation of state (EOS) [75-82].

CO ₂ +	N	T [K]	P [bar]	References
Decane	29	319.11-372.94	34.85-160.60	Jimenez-Gallegos <i>et al.</i> (2006)
Undecane	18	314.98-344.46	23.73-133.88	Camacho-Camacho <i>et al.</i> (2007)
Tetradecane	2	344.28	155.54-162.99	Gasem <i>et al.</i> (1989)
Pentadecane	22	293.15-353.15	5.60-139.40	Secuianu <i>et al.</i> (2010)
Hexadecane	12	314.14-333.13	80.65-148.70	D'Souza <i>et al.</i> (1988)
Octadecane	12	534.86-605.36	10.16-61.90	Kim <i>et al.</i> (1985)
Palmitic acid	10	423.20-473.20	10.10-50.70	Yau <i>et al.</i> (1992)
Oleic acid	16	313.15-353.15	101.70-300.20	Bharath <i>et al.</i> (1992)

Because high-pressure phase equilibrium data for the complex system OLP-CO₂ is not available in the literature, the proposed methodology was tested to simulate the thermodynamic modeling by de-acidification of olive oil, represented by a quaternary model mixture oleic acid-squalene-triolein-CO₂.

Table 5 summarizes the experimental high-pressure gaseous-liquid equilibrium data for the binary systems olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂ used to compute the binary interaction parameters.

Table 5. Experimental gaseous-liquid equilibrium data for the binary systems oleic acid-CO₂, squalene-CO₂, and triolein-CO₂ used to compute the binary interaction parameters of RK-Aspen equation of state (EOS) [82-86].

CO ₂ +	T [K]	P [bar]	N	References
Triolein	333.15, 353.15	200-500	8	Weber et al. (1999)
	313.15-333.15	153.4-310.0	8	Bharath et al. (1992)
Oleic acid	313-333	72.1-284.1	12	Zou et al. (1990)
	313.15-353.156	101.7-300.2	16	Bharath et al. (1992)
Squalene	313-333	100-350	11	Hernandez et al (2010)
	333.15-363.15	100-350	12	Brunner et al. (2009)

2.1.3.3. Schematic diagram of phase equilibria data correlation

The Aspen Properties® package program used for the regression of experimental phase equilibrium data described in Tables 4 and 5. Figure 1 illustrates the simplified schematic diagram of the main correlation steps of phase equilibria data for the binary system OLP compounds-i-CO₂, and the binary system olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂, performed by using the Aspen Properties®.

The program provides several options showing how to perform regression, including several different types of objective functions. The default objective function is the Maximum likelihood objective function, given by equation 1. To obtain the binary interaction parameters in Aspen Properties®, the following procedure was applied, regardless the type of system and model to which data will be correlated.

1. Choice of components;
2. Specification of the method (where the model applied for the regression of the experimental data is chosen);
3. Introduction or choice of experimental data (T-xy, P-xy, TP-x, T-x, TP-xy, T-xx, P-xx, TP-xx, TP-xy, etc.) depending on the type and information of the system; at this stage it is possible to either search for the compounds from the Aspen Properties® data base or enter experimental data manually;
4. Regression of data: In this step the type of parameter, the parameters (according to the coding of the program) to be adjusted/correlated, the initial estimate and the limits for the regression chosen.

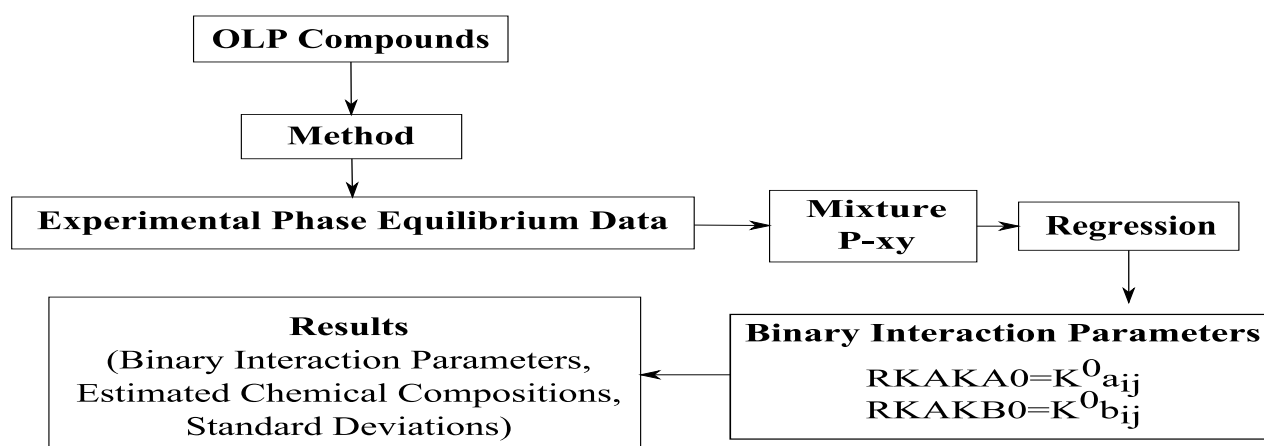


Figure 1. Simplified schematic diagram of the main correlation steps of phase equilibrium data for the binary system organic liquid products compounds-i-CO₂, and the binary system olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂, performed by using the Aspen Properties®.

3. Results and Discussions

3.1. Prediction of thermo-physical properties and the acentric factor of OLP compounds

3.1.1. Normal boiling temperature (T_b) of OLP compounds

The most indicated methods, consistent with the selection criteria described in section 2.1.2., adopted to estimate the normal boiling temperature (T_b) of hydrocarbons classes present in OLP illustrated in Table 6. For the n-alkanes and alkenes, the method by Marrero-Gani [66], provided the best correlation/regression to experimental data, while the method by Constantinou-Gani [64], shows the best correlation/regression for unsubstituted and substituted cyclics, and that by Joback and Reid [63], was the best for aromatics. Kontogeorgis and Tassios [87], reported that Joback and Reid [63] method was not suitable to estimate critical properties of alkanes of high molecular weight and selected Constantinou-Gani [64], as the best method.

Table 6. Selected methods to predict the normal boiling temperature (T_b) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), of all the compounds present in OLP, obtained by thermal catalytic cracking of palm oil at 450 °C, 1.0 atmosphere, with 10% (wt.) Na_2CO_3 [17].

Class of Hydrocarbons	N	ARD [%]	S [%]	R [%]	Methods
n-Alkanes	27	-2.806	1.943	6.797	Marrero-Gani
Alkenes	19	-0.848	1.206	5.396	Marrero-Gani
Unsubstituted cyclics	9	-2.001	4.815	13.720	Constantinou-Gani
Substituted cyclics	62	-0.546	2.208	10.604	Constantinou-Gani
Aromatics	28	-0.214	1.916	7.021	Joback

3.1.2. Critical temperature (T_c) of OLP compounds

Table 7 shows the selected methods to predict the critical temperature (T_c) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), present in OLP. The method by Marrero-Gani [66], is the most suitable for n-alkanes, alkenes, unsubstituted and unsubstituted cyclic hydrocarbons, as it showed the best correlation/regression to experimental data, while that by Constantinou-Gani [64], provided the best correlation/regression to experimental data for aromatics. Owczarek and Blazej [88] applied the methods by Joback and Reid [63] and Constantinou-Gani [64], to predict the critical temperature (T_c) of substituted and unsubstituted cyclic hydrocarbons, reporting deviations of 0.93% and 0.82%, respectively, when using the method by Joback and Reid [63], as well as deviations of 1.77% and 2.00%, respectively, with the method by Constantinou-Gani [64]. The results showed that computed deviations of substituted and unsubstituted cyclic hydrocarbons were 1.41% and 1.69%, respectively, when using the method by Joback and Reid [63], as well as 0.79% and 3.08%, with the method by Constantinou-Gani [64], higher than that described in Table 7, when using the method by Marrero-Gani [66]. The method by Constantinou-Gani [64] is the most suitable for aromatics. As by the estimation of normal boiling temperature (T_b), prediction of critical temperature (T_c) of aromatic hydrocarbons included also n-alkyl-benzenes, alkyl-benzenes, polyphenyls, as well as condensed polycyclic aromatics.

Table 7. Selected methods to predict the critical temperature (T_c) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), of all the compounds present in OLP, obtained by thermal catalytic cracking of palm oil at 450 °C, 1.0 atmosphere, with 10% (wt.) Na_2CO_3 [17].

Class of Hydrocarbons	N	ARD [%]	S [%]	R [%]	Methods
n-Alkanes	15	-0.685	0.157	0.496	Marrero-Gani
Alkenes	14	0.74	0.544	2.072	Marrero-Gani
Unsubstituted cyclics	7	-0.839	2.113	5.364	Marrero-Gani

Substituted cyclics	13	0.152	1.089	3.364	Marrero-Gani
Aromatics	31	-1.192	2.233	8.415	Constantinou-Gani

3.1.3. Critical pressure (P_c) of OLP compounds

The most indicated methods to estimate the critical pressure (P_c) of hydrocarbons functions present in OLP are illustrated in Table 8. For n-alkanes, the method by Marrero-Padillo [65], provided the best results, while that by Marrero-Gani [66], selected for alkenes. For unsubstituted cyclic, the method by Joback and Reid [63], was selected. For substituted cyclic, the method by Constantinou-Gani [64], was selected. By predicting the critical pressure (P_c) of aromatics, only the alkyl-benzenes were considered, being the method by Marrero-Gani [66], the best one. This is due to the high average relative deviation obtained for polycyclic condensates and poly-phenyls using all the methods described in Table 2, with ADR higher than 15%, reaching for some cases (m-terphenyl-Cas 92-06-8) 45%. In this sense, none of the methods evaluated showed good precision to estimate the critical pressure (P_c) of polycyclic condensates and poly-phenyls aromatic.

Table 8. Selected methods to predict the critical pressure (P_c) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), of all the compounds present in OLP, obtained by thermal catalytic cracking of palm oil at 450 °C, 1.0 atmosphere, with 10% (wt.) Na_2CO_3 [17].

Class of Hydrocarbons	N	ARD [%]	S [%]	R [%]	Methods
n-alkanes	17	3.749	2.12	6.996	Marrero-Gani
alkenes	16	0.353	2.781	10.809	Marrero-Pardillo
Unsubstituted cyclics	7	-0.47	2.355	6.593	Joback
Substituted cyclics	14	1.537	2.939	12.782	Constantinou-Gani
Aromatics	18	0.461	2.035	9.486	Marrero-Gani

3.1.4. Critical volume (V_c) of OLP compounds

Table 9 shows the selected methods to predict the critical volume (V_c) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), present in OLP. The method by Marrero-Gani [66], is the most suitable for n-alkanes and substituted cyclic hydrocarbons, as it showed the best correlation/regression to experimental data, while that Joback and Reid [63], selected for unsubstituted cyclic hydrocarbons. The method by Marrero-Pardillo [65], selected for alkenes, while that by Constantinou-Gani [64], provided the best correlation/regression to experimental data for aromatics.

Table 9. Selected methods to predict the critical volume (V_c) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), of all the compounds present in OLP, obtained by thermal catalytic cracking of palm oil at 450 °C, 1.0 atmosphere, with 10% (wt.) Na_2CO_3 [17].

Class of Hydrocarbons	N	ARD [%]	S [%]	R [%]	Methods
n-alkanes	8	-0.23	0.681	2.070	Marrero-Gani
alkenes	16	-0.113	1.210	4.013	Marrero-Pardillo
Unsubstituted cyclics	6	-1.024	1.359	2.215	Joback
Substituted cyclics	14	-0.318	4.832	12.717	Marrero-Gani
Aromatics	19	0.034	1.914	6.785	Constantinou-Gani

3.1.5. Acentric factor (ω) of OLP compounds

The selected methods to estimate the acentric factor (ω) of hydrocarbons classes present in OLP illustrated in Table 10. For n-alkanes and alkenes, the method by Han-Peng [68], provided the best results, while the indirect method by Vetere [70], was selected for unsubstituted cyclic, unsubstituted cyclic and aromatics.

Table 10. Selected methods to predict the acentric factor (ω) of hydrocarbons classes (n-alkanes, alkenes, unsubstituted cyclics, substituted cyclics, and aromatics), of all the compounds present in OLP, obtained by thermal catalytic cracking of palm oil at 450 °C, 1.0 atmosphere, with 10% (wt.) Na₂CO₃ [17].

Class of Hydrocarbons	N	ARD [%]	S [%]	R [%]	Methods
n-alkanes	16	0.033	1.943	7.703	Han-Peng
alkenes	15	0.976	5.518	20.825	Han-Peng
Unsubstituted cyclics	7	2.822	2.555	7.374	Vetere
Substituted cyclics	16	1.843	3.539	15.089	Vetere
Aromatics	14	1.323	2.105	9.39	Vetere

3.2. Thermodynamic modeling of phase equilibrium data for the binary system OLP compounds-*i*/CO₂

3.2.1. Estimation of thermo-physical (T_b), critical properties (T_c, P_c, V_c), and acentric factor (ω) of OLP compounds

Table 11 shows the estimated values of thermo-physical (T_b), critical properties (T_c, P_c, V_c), and acentric factor (ω) of OLP compounds, recommended for the main chemical compounds present in the OLP obtained by thermal-catalytic cracking of palm oil, as described by Mâncio *et al.* [17]. The prediction of the normal boiling temperature and critical properties of carboxylic acids and esters of carboxylic acids followed the recommendations of Araújo and Meireles [69], and for estimation of acentric factor (ω), the indirect method proposed by Ceriani *et al.* [89]. This method makes use of group contributions with high similarities to the molecular structure of carboxylic acids and esters of carboxylic acids. In addition, the method proposed by Ceriani *et al.* [89], also applied for estimation of critical properties of ketones, while the method of Nikitin *et al.* [89], applied for alcohols.

Table 11. Estimated/Predicted values of thermo-physical (T_b), critical properties (T_c, P_c, V_c), and acentric factor (ω) of chemical compounds present in OLP obtained by thermal-catalytic cracking of palm oil, as described by Mâncio *et al.* [17].

Chemical Compounds	T _b [K]	T _c [K]	P _c [bar]	V _c [cm ³ /mol]	ω
Metil-Cyclooctane	446.111 ^b	639.678 ^c	24.958 ^b	468.72 ^c	0.3794 ^h
1-Butyl-1-Cyclohexene	457.679 ^b	593.736 ^c	24.124 ^b	515.94 ^c	1.0313 ^h
3-Isobutyl-1-Cyclohexene	439.701 ^b	588.010 ^c	23.996 ^b	518.05 ^c	0.7739 ^h
1-Decene	440.000 ^a	615.724 ^c	22.200 ^a	584.00 ^a	0.4869 ^f
Decane	447.200 ^a	617.70 ^a	21.100 ^a	594.89 ^c	0.4920 ^a
1-Hexil-Cyclopentene	476.755 ^b	583.790 ^c	22.342 ^b	522.98 ^c	1.6624 ^h
1-Undecene	466.000 ^a	636.280 ^c	20.073 ^d	638.00 ^d	0.5313 ^f
(E)-2-Undecene	469.338 ^c	639.873 ^c	16.116 ^d	689.90 ^d	0.5356 ^f
(Z)-2-Undecene	469.338 ^c	639.873 ^c	16.116 ^d	689.90 ^d	0.5356 ^f
Undecane	469.080 ^a	639.00 ^a	19.500 ^a	651.17 ^c	0.5300 ^a
1-Dodecene	486.200 ^a	655.158 ^c	19.300 ^a	694.60 ^d	0.5747 ^f
1-Tridecene	505.000 ^a	672.609 ^c	17.047 ^d	751.20 ^d	0.6171 ^f
Cyclotridecane	507.685 ^b	739.275 ^c	23.726 ^e	641.50 ^e	0.2895 ^h
Tridecane	508.620 ^a	675.00 ^a	16.800 ^a	763.73 ^c	0.6170 ^a

1-Octyl-Cyclohexene	494.340 ^b	673.018 ^c	20.150 ^b	741.06 ^c	0.5579 ^h
1-Tetradecene	524.200 ^a	688.836 ^c	15.785 ^d	807.80 ^d	0.6585 ^f
Cyclotetradecane	522.830 ^b	756.412 ^c	17.625 ^b	689.50 ^e	0.1939 ^h
Tetradecane	523.000 ^a	693.00 ^a	16.470 ^c	830.00 ^a	0.6430 ^a
1-Nonyl-1-Cyclohexene	539.343 ^b	689.216 ^c	15.891 ^b	797.34 ^c	0.8912 ^h
1-Pentadecene	541.540 ^a	703.998 ^c	14.657 ^d	864.40 ^d	0.6990 ^f
Nonylcyclohexane	545.000 ^a	728.078 ^c	16.056 ^b	814.74 ^c	0.5544 ^h
Cyclopentadecane	536.929 ^b	772.366 ^c	20.755 ^e	737.50 ^e	0.2864 ^h
Pentadecane	540.000 ^a	708.00 ^a	14.800 ^a	876.29 ^c	0.6860 ^a
(Z)-7-Hexadecene	560.902 ^c	734.435 ^c	15.046 ^d	1112.2 ^d	0.7426 ^f
(Z)-3-Hexadecene	560.902 ^c	734.435 ^c	15.046 ^d	1112.2 ^d	0.7426 ^f
1-Hexadecene	547.200 ^a	703.998 ^c	13.647 ^d	921.00 ^d	0.7387 ^f
Cyclohexadecane	550.118 ^b	787.290 ^c	19.475 ^e	785.50 ^e	0.2816 ^h
Hexadecane	554.000 ^a	723.00 ^a	14.000 ^a	932.57 ^c	0.7170 ^a
1-Heptadecene	559.440 ^c	731.631 ^c	12.737 ^d	977.60 ^d	0.7776 ^f
(E)-9-Octadecene	585.099 ^c	758.833 ^c	13.052 ^d	1225.4 ^d	0.8194 ^f
Octadecane	589.300 ^a	747.000 ^a	12.950 ^a	1045.13 ^c	0.8178 ^f
(E)-9-Eicosene	591.816 ^b	769.696 ^c	11.429 ^d	1338.6 ^d	0.8933 ^f
(Z)-9-Tricosene	620.891 ^b	800.665 ^c	9.508 ^d	1508.4 ^d	0.9993 ^f
Caproic Acid	477.000 ^a	660.200 ^a	33.800 ^a	413.00 ^a	0.7300 ^a
Glycerol	563.150 ^a	850.000 ^a	75.000 ^a	-	0.5130 ^a
N-Nonanoic Acid	527.150 ^a	710.700 ^a	25.140 ^a	562.89 ^b	0.7720 ^a
Capric Acid	530.000 ^a	722.100 ^a	22.500 ^a	618.65 ^b	0.8060 ^a
Lauric Acid	571.000 ^a	742.68 ^b	19.142 ^b	730.17 ^b	0.8689 ^g
Myristic Acid	588.311 ^b	762.508 ^b	16.356 ^b	841.69 ^b	0.9615 ^g
2-Nonadecanone	396.280 ^e	552.195 ^e	26.625 ^e	557.50 ^e	0.5575 ^h
Ethyl Palmitate	615.350 ^a	822.849 ^e	13.577 ^b	1065.50 ^c	0.8980 ^g
Octadecan-4-one	373.400 ^e	52.357 ^e	29.473 ^e	501.50 ^e	0.5698 ^h
Palmitic Acid	612.150 ^a	780.381 ^b	14.177 ^b	953.21 ^b	1.0281 ^g
Z-10-Octadecene-1-ol Acetate	723.65 ^d	896.254 ^e	12.6987 ^c	1158.27 ^b	0.9638 ^h
1-Eicosanol	742.70 ^d	808.000 ⁱ	11.500 ⁱ	1176.23 ^c	0.9100 ⁱ
Ethyl Oleate	717.050 ^e	888.080 ^e	12.699 ^b	1163.90 ^c	0.9009 ^g
Linoleic Acid	626.791 ^b	798.356 ^b	12.935 ^b	1032.51 ^b	0.9969 ^g
Oleic Acid	626.807 ^b	797.504 ^b	12.684 ^b	1048.62 ^b	1.0449 ^g
Stearic Acid	626.824 ^b	796.648 ^b	12.440 ^b	1064.73 ^b	1.0932 ^g
8-Octadecanone	372.700 ^e	525.993 ^e	30.933 ^e	492.50 ^e	0.5555 ^h

a-Yaws; *b*-Constantinou-Gani; *c*-Marrero-Gani; *d*-Marrero-Pardillo; *e*-Joback; *f*-Han-Peng; *g*-Ceriani; *h*-Vetere; *i*-Nikitin

3.2.2. Thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of olive oil key (oleic acid, squalene, triolein) compounds

The estimated values of thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of olive oil key (oleic acid, squalene, triolein) compounds summarized in Table 12. The values for the thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of olive oil model mixture compounds (oleic acid, squalene, triolein) are those predicted by the authors described in Table 5.

Table 12. Estimated/Predicted values of thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) of olive oil key (oleic acid, squalene, triolein) compounds [82-86].

Compounds	Cas Number	MW	T_b [°C]	T_c [°C]	P_c [kPa]	V_c [m ³ /kmol]	ω [-]
Triolein	122-32-7	885.00	616.7	673.9	468.2	3.022	1.686
Oleic acid	122-80-1	282.2	353.7	579.4	1388.0	1.101	1.0787
Squalene	7683-64-9	410.7	401.2	564.9	653.0	2.052	1.398

3.2.3. Estimation of RK-Aspen EOS temperature-independent binary interaction parameters for the binary systems hydrocarbons-i-CO₂ and carboxylic acids-i-CO₂

Table 13 presents the RK-Aspen EOS temperature-independent binary interaction parameters adjusted with experimental phase equilibrium data for the binary systems hydrocarbons-i-CO₂ and carboxylic acids-i-CO₂, as well as the absolute mean deviation (AAD) between experimental and predicted compositions for both coexisting liquid and gaseous phases. The regressions show that RK-Aspen EOS was able to describe the high-pressure gaseous-liquid experimental phase equilibrium data for all the systems investigated.

Table 13. RK-Aspen EOS temperature-independent binary interaction parameters adjusted with experimental phase equilibrium data for the binary systems hydrocarbons-i-CO₂ and carboxylic acids-i-CO₂.

CO ₂ +	T [K]	$k_{aij} = k_{aij}^0$	$k_{bij} = k_{bij}^0$	AADx	AADy
Undecane	314.98	0.116458	-0.008014	0.0029	0.0003
	344.46	0.103282	-0.029465	0.0030	0.0036
Tetradecane	344.28	0.099874	-0.000546	0.0003	0.0011
Pentadecane	313.15	0.093344	0.026454	0.0125	0.0020
	333.15	0.101805	0.014904	0.0067	0.0030
Hexadecane	314.14	0.083111	-0.075317	0.0117	0.0090
	333.13	0.082146	-0.081056	0.0013	0.0034
Octadecane	534.86	0.246616	0.073306	0.0010	0.0024
	605.36	0.107125	0.015525	0.0002	0.0064
Palmitic acid	423.20	-0.179556	-0.042625	0.0037	8.93E-05
	473.20	-0.059218	-0.013329	0.0008	0.0002
Oleic acid	313.15	0.110902	0.132527	0.0039	0.0031
	333.15	0.116604	0.054485	0.0039	0.0035
	353.15	0.117892	0.049413	0.0049	0.0046

3.2.4. Estimation of RK-Aspen EOS temperature-independent binary interaction parameters for the binary systems olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂

Table 14 summarizes the RK-Aspen EOS temperature independent binary interaction parameters adjusted to experimental high-pressure phase equilibria of olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂, used as *test system to simulate the thermodynamic modeling by de-acidification of olive oil, represented by a quaternary model mixture oleic acid-squalene-triolein-CO₂*.

Table 14. RK-Aspen EOS temperature-independent binary interaction parameters adjusted with experimental phase equilibrium data for the binary systems hydrocarbons-i-CO₂ and carboxylic acids-i-CO₂.

CO ₂ +	T (K)	$k_{aij} = k_{aij}^0$	$k_{bij} = k_{bij}^0$	AAD _x	AAD _y
Triolein	313.15 ^(a)	0.071209	0.099779	0.0094	0.0027
	333.15 ^(a)	0.077653	0.096221	0.0126	0.0030
	333.15 ^(b)	0.078059	0.083746	0.0088	0.0003
	353.15 ^(b)	0.103763	0.132745	0.0050	0.0001
Squalene	333.15 ^(c)	0.054090	-0.023325	0.0022	0.0025
	363.15 ^(c)	0.047825	-0.032640	0.0031	0.0014
	313 ^(f)	0.065395	-0.030832	0.0151	0.0016
	333 ^(f)	0.067249	-0.032589	0.0128	0.0013
Oleic acid	313.15 ^(a)	0.115801	0.130956	0.0199	0.0031
	333.15 ^(a)	0.116604	0.054485	0.0084	0.0035
	353.15 ^(a)	0.117892	0.049413	0.0062	0.0046
	313.15 ^(d)	0.070093	-0.006360	0.0094	0.0051
	333.15 ^(d)	0.089088	0.041100	0.0002	0.0067

a-Bharath et al. (1992), b-Weber et al. (1999), c-Brunner et al. (2009), d-Zou et al. (1990), f-Hernandez et al. (2010).

3.2.4.1. Equation of state (EOS) modeling for the binary systems olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂

The thermodynamic modeling for the binary systems olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂ performed with RK-Aspen EOS with the van der Waals mixing rules and RK-Aspen combining rules for two temperature-independent binary interaction parameters. The EOS modeling described in form P-x_{CO2}-y_{CO2} diagram showing a comparison between predicted and experimental high-pressure equilibrium data for the binary systems oleic acid-CO₂ (Bharath et al., 1992), squalene-CO₂ (Brunner et al., 2009), and triolein-CO₂ (Weber et al., 1999), as shown in Figures 2, 3, and 4, respectively. The regressions show that RK-Aspen EOS was able to describe the high pressure equilibrium data for the binary systems olive oil key (oleic acid, squalene, triolein) compounds-i-CO₂.

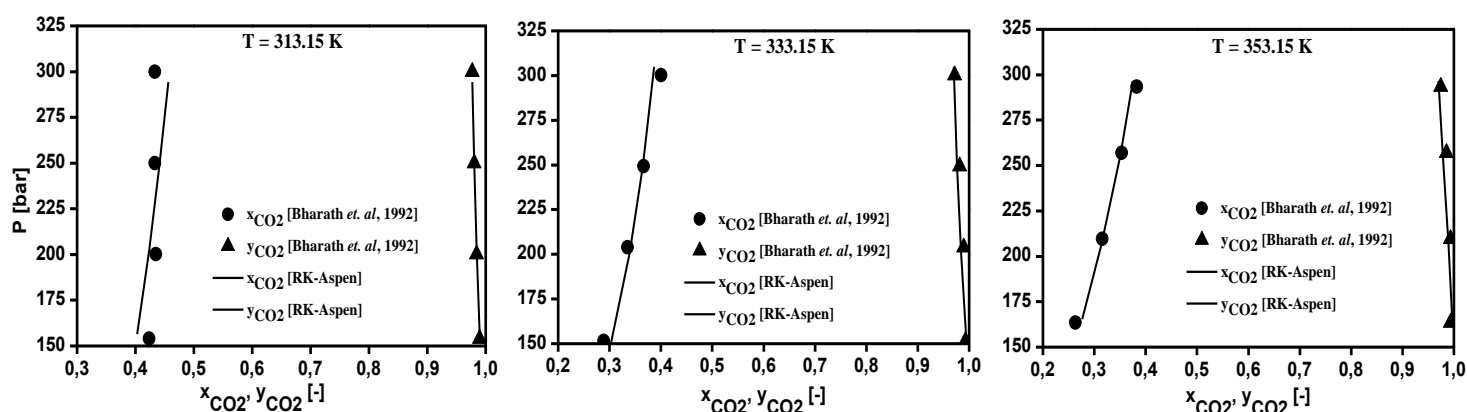


Figure 2. Experimental and predicted high-pressure phase equilibrium for the system oleic acid-CO₂ (Bharath et al., 1992).

k_{aij}^0	-1.78375	1.00000	-2.19466	-1.26916	0.06593	-0.90195	0.0017	2.8E-05
k_{bij}^0	1.97388	0.32731	-3.32627	-0.36925	0.31781	-0.87789		
FFA in feed = 5.2 [wt.%], T[K] = 338								
k_{aij}^0	2.44416	-0.68874	2.65877	-0.07842	0.00445	0.40698	3.0E-07	2.0E-08
k_{bij}^0	2.16063	0.99919	1.77156	0.08648	0.37099	-1.22870		
FFA in feed = 5.2 [wt.%], T[K] = 353								
k_{aij}^0	0.05504	0.13002	0.14571	0.16947	0.08930	0.43896	0.0058	7.4E-07
k_{bij}^0	0.12297	-0.66975	0.00107	-0.91096	0.18358	0.66131		
FFA in feed = 7.6 [wt.%], T[K] = 313								
k_{aij}^0	-0.39597	0.95245	-0.41348	-0.40686	0.06993	-0.16959	0.0010	0.0002
k_{aij}^0	0.74176	-4.75749	-0.76430	0.70767	0.27402	0.22365		
FFA in feed = 15.3[wt.%], T[K] = 338								
k_{aij}^0	1.89568	0.99648	2.17462	0.31810	0.06235	-0.22787	0.0007	6.9E-05
k_{aij}^0	0.75657	0.51874	2.50669	0.92458	0.20835	0.54779		

State conditions (T, P) by the experimental high-pressure equilibrium data for the multi-component olive oil-CO₂, described in Table 16

Table 16. State conditions (T, P) by high-pressure phase equilibrium data for the system *olive oil*-CO₂ [91].

FFA [wt.%]	T [K]	P [bar]	N	Reference
2.9	313	138-275	4	Simões and Brunner (1996)
	323	182-257	3	
5.2	338	190-280	2	
	353	210-298	3	
7.6	313	180-281	3	
	323	179-212	2	
15.3	313	180-302	3	
	338	21-259	2	
	353	212-303	3	

Table 17 presents the average absolute deviation (AAD) between the predicted and experimental high-pressure phase equilibrium data for the model systems *oleic acid*(1)-*squalene*(3)-*triolein*(2)-CO₂(4).

Table 17. The average absolute deviation (AAD) between the predicted and experimental high-pressure phase equilibrium data for the model systems *oleic acid*(1)-*squalene*(3)-*triolein*(2)-CO₂(4).

AAD									
FFA in feed [wt.%]	T [K]	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
2.9	313	0.0062	0.1906	0.0017	0.1828	0.0000	0.0002	0.0000	0.0003
2.9	323	0.0164	0.2310	0.0028	0.2118	0.0020	0.0027	0.0006	0.0027
5.2	338	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
5.2	353	0.0215	0.7240	0.0033	0.7082	0.0001	0.0001	0.0000	0.0001
7.6	313	0.0164	0.1274	0.0014	0.1097	0.0093	0.0225	0.0009	0.0324
15.3	338	0.0090	0.0908	0.0003	0.0816	0.0053	0.0059	0.0000	0.0112

Table 18 presents the RK-Aspen EOS temperature independent binary interaction parameters adjusted in this work to experimental high-pressure equilibrium for the system olive oil-CO₂ at 313 K with 2.9 and 7.6 [wt.%] FFA. The RK-Aspen EOS was able to describe the high-pressure phase equilibria of multicomponent system olive oil-CO₂ [91], showing RMSD between 3E-07 to 0.0138 for the liquid phase and between 0.0009 to 2E-04 for the gaseous phase, by considering the system was represented by the multicomponent model mixture triolein-squalene-oleic acid-CO₂.

Table 18. Estimated RK-Aspen-EOS binary interaction parameters for multicomponent system FFA (oleic acid)(1)-Triglyceride (triolein)(2)-Squalene(3)-CO₂(4).

k_{ij}	1-2	1-3	1-4	2-3	2-4	3-4	RMSD _x	RMSD _y
FFA in feed = 2.9 and 7.6 [wt.%], T [K] = 313								
k_{aij}^0	-0.150477	-0.297646	-0.111520	-0.602362	0.074580	-0.802333	0.0138	0.0009
k_{bij}^0	0.286959	-0.614753	-0.372917	0.992085	0.127803	-0.803741		

The distribution coefficients- K_i of key compounds by the experimental high-pressure phase equilibria for the multicomponent system olive oil-CO₂, described on solvent free basis, as shown in Table 19. Table 19 presents the experimental distribution coefficients of FFA (1), triglyceride (2), and squalene (3) and the estimated distribution coefficients computed using the binary interaction parameter presented in Table 15. The results show the precision of RK-Aspen EOS to describe the multicomponent system for the state conditions (T, P), and free fatty acid (FFA) content in feed. The distribution coefficients described on a solvent free basis provide information about the phase in which the compounds are preferably enriched in the extract ($K_i > 1$) or in the bottoms ($K_i < 1$). Figures 5, 6, and 7 show the distribution coefficients for the key compounds of olive oil computed on CO₂ free basis. The results show that FFA and squalene are preferably enriched in the extract ($K_i > 1$), while the triolein is enriched in the bottoms ($K_i < 1$) by de-acidification of olive oil using SC-CO₂ in countercurrent packed columns.

Table 18. The distribution coefficients- K_i of key compounds FFA (1), triglyceride (2), and squalene (3), expressed on a solvent free basis, by the experimental high-pressure phase equilibria for the multicomponent system olive oil-CO₂.

FFA in feed [wt.%]/T [K]	P [bar]	$K_1 \times 10^2$		$K_2 \times 10^2$		$K_3 \times 10^2$	
		exp	est	exp	est	exp	est
2.9/313	138	1.09	1.08	0.09	0.09	1.71	1.71
	176	2.88	2.87	0.36	0.36	4.27	4.26
	208	4.01	4.01	0.52	0.52	4.75	4.73
	275	4.50	4.51	0.81	0.81	5.95	5.98
2.9/323	182	1.93	1.97	0.10	0.10	2.54	2.55
	206	2.68	2.83	0.25	0.25	4.03	4.30
	257	4.17	3.99	0.70	0.71	4.77	4.59
5.2/338	190	1.08	1.08	0.08	0.08	1.26	1.26
	280	4.59	4.59	0.88	0.88	5.34	5.34
5.2/353	210	2.89	2.87	0.18	0.18	2.11	2.11
	260	4.76	4.80	0.44	0.44	3.07	3.10
	298	7.11	7.08	0.88	0.86	5.13	5.17
7.6/313	180	2.32	2.48	0.28	0.28	3.45	3.67
	208	3.33	3.04	0.57	0.54	4.06	3.83
	281	4.64	4.73	0.90	0.96	5.02	4.95
15.3/338	215	2.65	2.71	0.54	0.55	7.60	7.61
	259	2.67	2.60	1.08	1.07	5.16	5.17

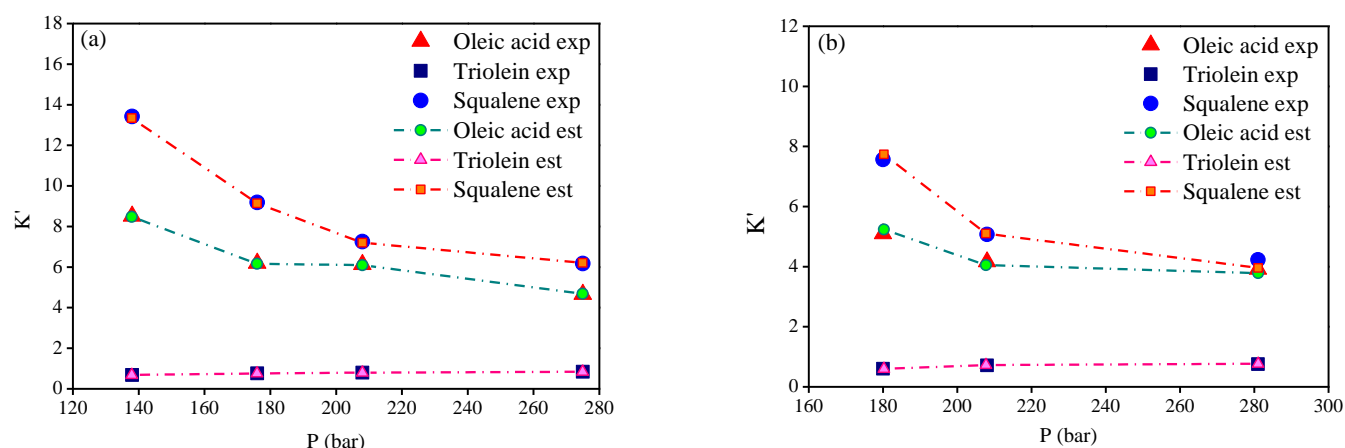


Figure 5. Experimental and estimated distribution coefficients K_i , expressed in CO₂-free basis, at 313 K with (a) 2.9 and (b) 7.6 [wt.%] of FFA.

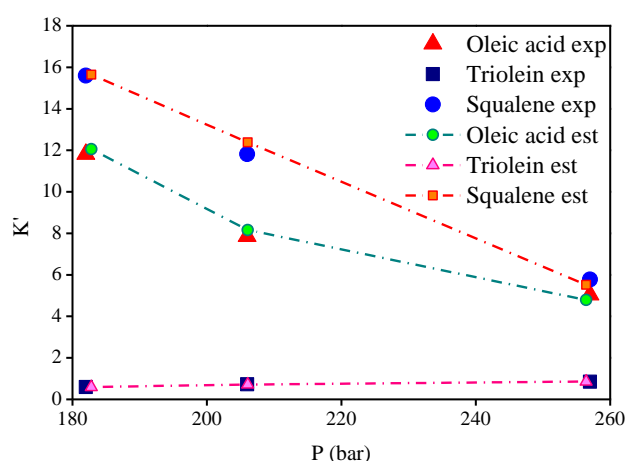


Figure 6. Experimental and estimated distribution coefficients K_i , expressed in CO₂-free basis, at 323 K with 2.9 [wt.%] of FFA.

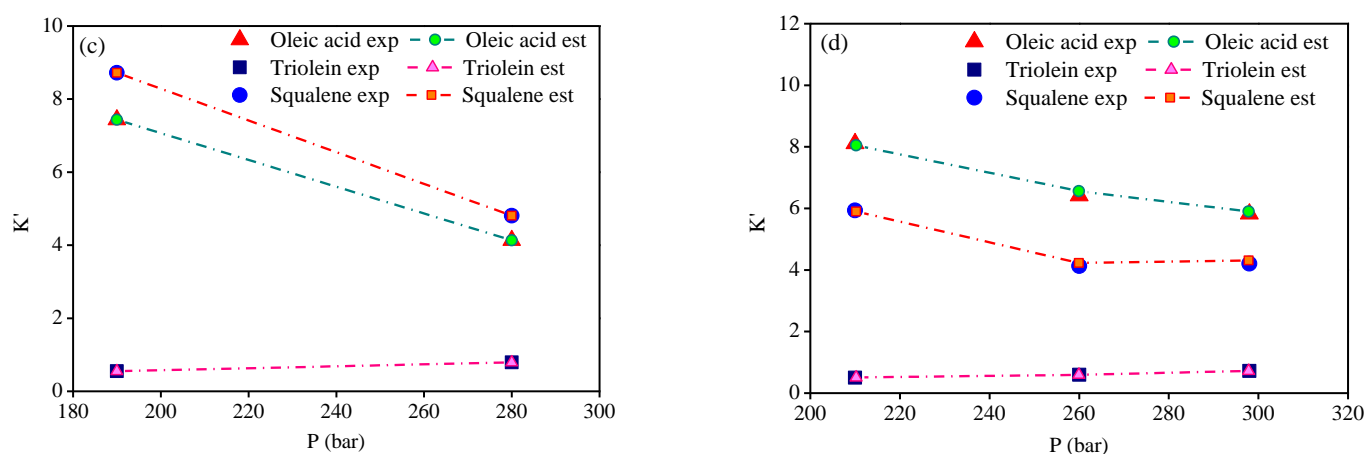


Figure 7. Experimental and estimated distribution coefficients K_i , expressed in CO₂-free basis, at (a) 338 and (b) 353 K with 5.2 [wt.%] of FFA.

The proposed methodology proved to simulate with high accuracy the thermodynamic modeling by de-acidification of olive oil, represented by a quaternary model mixture oleic acid-squalene-triolein-CO₂, and hence can be applied to simulate the fractionation of OLP in multistage counter-current absorber/stripping columns using SC-CO₂ as solvent, with Aspen-Hysys.

5. Conclusions

The EOS modeling described in form P - x_{CO_2} , y_{CO_2} diagram for the binary systems oleic acid- CO_2 (Bharath et al., 1992), squalene- CO_2 (Brunner et al., 2009), and triolein- CO_2 (Weber et al., 1999), shows that RK-Aspen EOS was able to describe the high pressure equilibrium data for the binary systems olive oil key (oleic acid, squalene, triolein) compounds- i - CO_2 .

The RK-Aspen EOS was able to describe the high-pressure phase equilibria of multicomponent system olive oil- CO_2 [91], showing RMSD between $3E-07$ to 0.0138 for the liquid phase and between 0.0009 to $2E-04$ for the gaseous phase, by considering the system was represented by the multicomponent model mixture triolein-squalene-oleic acid- CO_2 .

The proposed methodology proved to simulate with high accuracy the thermodynamic modeling by de-acidification of olive oil, represented by a quaternary model mixture oleic acid-squalene-triolein- CO_2 , and hence can be applied to simulate the fractionation of OLP in multistage counter-current absorber/stripping columns using SC- CO_2 as solvent, with Aspen-Hysys.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Graphics G1-G4: Relative deviation of predicted/estimated thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) for n-alkanes.

Author Contributions: The individual contributions of all the co-authors are provided as follows: Elinéia Castro Costa contributed with *formal analysis and writing—original draft preparation*, Welisson de Araújo Silva contributed with *EOS modeling*, Eduardo Gama Ortiz Menezes contributed with thermo-physical (T_b), critical properties (T_c , P_c , V_c), and acentric factor (ω) computations, Vânia Maria Borges Cunha contributed with computation of binary interaction parameters with Aspen-Hysys, Marcilene Paiva da Silva contributed with computation of binary interaction parameters with Aspen-Hysys, Marcelo Costa Santos contributed with *thermal-catalytic cracking experiments*, Andréia de Andrade Mâncio with *thermal-catalytic cracking experiments*, Sílvio Alex Pereira da Mota OLP chemical composition, Marilena Emmi Araújo contributed with *supervision, conceptualization, and data curation*, and Nélito Teixeira Machado contributed with *supervision, conceptualization, and data curation*. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by CAPES-Brazil, grant number: 207325/2014-6.

Acknowledgments: I would like to acknowledge Prof. Dr. Ernesto Reverchon for his marvelous contribution to supercritical fluid technology.

Conflicts of Interest: The authors declare no conflict of interest.

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